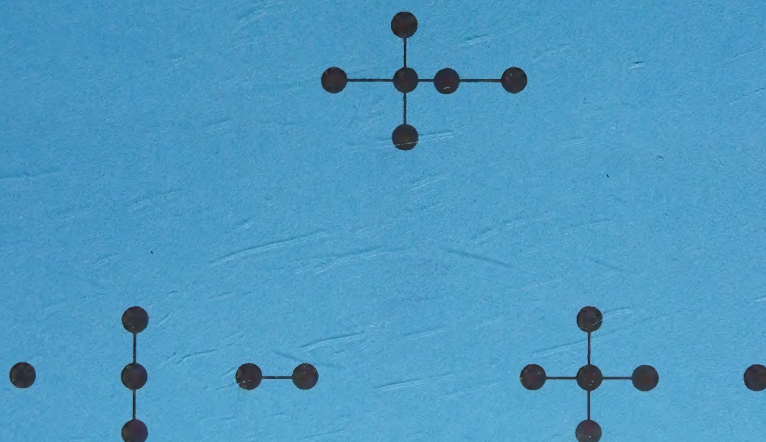


SYMMETRY REQUIREMENTS FOR SUBSTITUTION AND REDOX PROCESSES OF SQUARE-PLANAR HALIDE COMPLEXES

Lars-Fride Olsson



Lund 1980



Symmetry Requirements for Substitution and Redox
Processes of Square-planar Halide Complexes

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Abstract The <u>kinetics</u> of <u>formation/cleavage</u> of a <u>dimeric iodide-bridged palladium(II) complex</u>, of the formation of a 1:1 complex between <u>platinum (II)</u>, <u>palladium(II)</u> and <u>iodide</u> and of the <u>reduction</u> of <u>gold(III) chloro</u> and <u>bromo complexes</u> by <u>iodide</u> have been studied by <u>stopped-flow</u> and <u>conventional spectrophotometry</u>. <u>Charge transfer</u> and <u>d-d spectra</u> of <u>tetrahalide</u> and <u>mixed aqua-halide complexes</u> of <u>platinum(II)</u>, <u>palladium(II)</u> and <u>gold(III)</u> have been analyzed and spectral assignments are suggested. For <u>palladium(II)</u> and <u>gold(III)</u> the charge-transfer bands are described as <u>ligand-to-metal charge-transfer</u>, but for <u>platinum(II)</u> they are better described as due to charge-transfer from metal d to a mixture of metal and ligand p-orbitals. This indicates a difference in the electronic structure between <u>palladium(II)</u> and <u>gold(III)</u> on the one hand and <u>platinum(II)</u> on the other. The interpretation of the spectra in terms of the energy and symmetry of the excited states has been utilized for a discussion of the <u>mechanisms</u> for <u>ligand substitutions</u> and <u>redox reactions</u> by the use of the <u>second-order Jahn-Teller effect</u>. The <u>trans-effect</u> and its subdivision into σ- and π-effects can be explained. According to the suggested interpretation, the mechanism for <u>reductive elimination</u> can be considered as a special case of the σ-trans-effect. The difference in reactivity of five to six orders of magnitude between <u>gold(III)</u> and <u>palladium(II)</u> on the one hand and <u>platinum(II)</u> on the other, is also consistent with the proposed differences in electronic structures.		
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INTRODUCTION

This thesis will discuss the kinetic and spectroscopic properties of the square-planar aqua-halide complexes of palladium(II), platinum(II) and gold(III). The main purpose has been an attempt to correlate information from UV and visible absorption spectra and symmetry properties of these complexes with reactivity and reaction mechanisms.

The work by Elding and coworkers¹⁻⁴ on mononuclear ligand substitution and redox reactions of chloride and bromide systems has been extended to include iodide systems. All the experimental results are described in Appendix 1 and in the following papers. They will be referred to by their Roman numerals:

I L.I. Elding and L.F. Olsson

Ligand Substitution Processes in Platinum(II) and Palladium(II) Iodide Systems.

II L.I. Elding and L.F. Olsson

Kinetics, Mechanism and Equilibrium for Formation/Cleavage of a Dinuclear Iodide-Bridged Complex of Palladium(II).
Inorg. Chem. 16 (1977) 2789.

III L.I. Elding and L.F. Olsson

Kinetics and Mechanism for Reduction of Tetrachloro- and Tetrabromoauroate(III) by Iodide.

IV L.I. Elding and L.F. Olsson

Electronic Absorption Spectra of Square-Planar Chloro-Aqua and Bromo-Aqua Complexes of Palladium(II) and Platinum(II).

J. Phys. Chem. 82 (1978) 69.

Macroscopically, the spectral and kinetic properties of a chemical species are seemingly unconnected. In a description on the molecular level in terms of electronic transitions and mechanisms, respectively, both are based on a common origin, however, the symmetry and energy of a few active orbitals. A discussion of elementary chemical processes based on these concepts thus necessitates a knowledge of the electronic structure of the species involved. At present, this structure can be described adequately only by the molecular orbital theory. No quantitative and reliable quantum-chemical methods of calculation for the complexes considered here are available so far. To gain further insight into the electronic structure it is necessary to study the electronic absorption spectra and to interpret them in terms of energy and symmetry of the molecular orbitals (paper IV).

Mechanisms of inorganic chemical reactions have until recently mainly been discussed on the basis of rate laws and product analysis. During the seventies Pearson⁵ published a number of papers culminating in 1976 with the book⁶ "Symmetry Rules for Chemical Reactions" where he showed how the so-called second-order Jahn-Teller effect proposed in a paper by Bader⁷ could be used to gain information about reaction mechanisms. A reaction involves a change in positions of some of the atoms of the reactants. In its initial stage it can be described as a distortion, which can, by group-theory, be resolved into a number of component motions (cf. Fig. 6.1). These can be classified according to the manner in which the displacement vectors transform under the symmetry operations of the group describing the molecular geometry. Even the state wave-functions can be symmetry classified in the same manner (labelled with a so-called symmetry species). Irrespectively of how a complex is distorted, the geometrical change is accompanied by a change in the wave-function. By second-order perturbation theory both the change in the wave-function and its energy may be derived and the following rule will emerge:

The energy increase for a motion of a particular symmetry

species is low, if low lying excited electronic states are present, whose wave-functions have related symmetry species. Therefore, if these symmetry and energy properties of a complex are known, they will suggest possible atomic displacements which may correspond to a reaction path, at least in its initial stage.

Once the geometry of a complex is known the possible motions can be classified. A knowledge of the energy eigenvalues and symmetry species of the excited state wave-functions can be inferred from different types of spectral measurements. For a description of a chemical change, bond-making and -breaking are essential concepts. They can be incorporated into the theory by expressing the state wave-functions as anti-symmetrized products of molecular orbitals. Accordingly, the symmetry species and energies of the orbitals corresponding to σ -bonding and -antibonding are essential.

2. EXPERIMENTAL

Experimental details are given in the respective papers. Iodide systems of gold, palladium and platinum are much more complicated to handle experimentally than the chloride and bromide systems. This is mainly due to redox reactions and low solubility.

It is well-known that iodide is easily oxidized by air in aqueous solution, especially at low pH. The two products, iodine and the triiodide ion (present together with iodine when $[I^-] \gtrsim 5 \cdot 10^{-4} M$) might oxidize Pt(II) to Pt(IV) and the absorption spectrum of the triiodide ion will interfere with those of the metal-iodide complexes (II, Fig. 1). It is thus essential to suppress oxidation of iodide. This is accomplished by excluding oxygen (air), keeping low acidity and using chemicals with very low contents of oxidizing impurities. It is not possible to add reductants such as sulphite or thiosulphate because these form strong complexes with platinum and palladium and can reduce gold(III)⁸. At high

iodide concentrations, where the complexes AuI_2^- , PtI_4^{2-} , PdI_4^{2-} and $\text{Pd}_2\text{I}_6^{2-}$ predominate, neutral or only slightly acidic solutions can be used (II, III), but at lower concentrations of iodide (I) the acidity must be rather high to prevent the hydrolysis of the various aqua-halide species which are then formed. This necessitates the continuous nitrogen flow described in I.

The other complication is due to the low solubility of $\text{PdI}_2(\text{s})$ and $\text{PtI}_2(\text{s})$. These precipitate quantitatively, $\text{PdI}_2(\text{s})$ within the time of mixing a palladium solution with an equinormal iodide solution and $\text{PtI}_2(\text{s})$ somewhat slower. (This complication is absent in the case of $\text{Au}(\text{III})$ where there is instead a reduction to $\text{Au}(\text{I})$, which is faster than the precipitation, cf. III). The possibility to prepare metastable supersaturated solutions was also restricted (II). As a curiosity it may be mentioned that the way of mixing two solutions was essential for the stability of the supersaturated solution (II). Dilution of a "concentrated" $\text{PdI}_4^{2-}/\text{I}^-$ -solution by a 1 M $\text{NaClO}_4(\text{aq})$ -solution to produce a supersaturated $\text{Pd}_2\text{I}_6^{2-}/\text{PdI}_4^{2-}/\text{I}^-$ -solution, had to be made by quickly transferring a small volume of the former into a large volume of the latter. Reversing the mixing procedure quickly gave a colloidal solution and finally precipitation of $\text{PdI}_2(\text{s})$.

The low solubility has prevented the study of any reactions involving $\text{trans-PdI}_2(\text{aq})$, $\text{cis-PdI}_2(\text{aq})$ and $\text{PdI}_3^-(\text{aq})$ and the corresponding two latter Pt-complexes. It also made necessary the use of substrate concentrations in the μM range and very pure chemicals, for instance thoroughly recrystallized supporting electrolyte (NaClO_4).

3. RATE LAWS AND MECHANISMS

3.1. Halide anation and dimerization

The rate law for the reaction between iodide and tetra aqua platinum(II) and palladium(II) (I) is given by the two-term

equation

$$\text{RATE} = k_1[\text{M}(\text{H}_2\text{O})_4^{2+}][\text{I}^-] + k_{-1}[\text{MI}(\text{H}_2\text{O})_3^+] \quad (3.1)$$

k_1 is the rate constant for the forward (anation) reaction of $\text{M}(\text{H}_2\text{O})_4^{2+}$ ($\text{M} = \text{Pd}, \text{Pt}$) and k_{-1} that for the back (acid hydrolysis) reaction. The reaction has been studied under pseudo first-order conditions i.e. with one of the reactants (complex or iodide) in large excess. In this case eq. (3.1) simplifies to

$$\text{RATE} = (k_{-1} + k_1 \cdot C)(X - X_\infty) \quad (3.2)$$

where C is the concentration of the reactant in excess and X that of the other (X_∞ is the concentration of X at equilibrium and is usually negligible).

Equation (3.1) has been interpreted in terms of an associative mechanism involving a five-coordinated activated complex. Elding^{1,4} and Gröning³ have discussed such a mechanism in the case of the aqua chloro and bromo complexes of square-planar $\text{Pt}(\text{II})$, $\text{Pd}(\text{II})$ and $\text{Au}(\text{III})$. As expected (cf. ref. 4(c) Table VII) the reaction between the tetra aqua platinum(II) and iodide is approximately 10^5 times slower than the corresponding reaction involving palladium(II).

The model where the activated complex consists of a central metal atom surrounded by five ligands can also be applied to the formation and cleavage of the dinuclear complex described in II. According to the suggested mechanism (Fig. 3.1) the two metal atoms are simultaneously assumed to be five-coordinated in the transition state (Fig. 3.1 stage C). If the rate-determining steps are assumed to be the formation or cleavage (to PdI_4^{2-} and/or $\text{PdI}_3(\text{H}_2\text{O})^-$) of the dinuclear complex $\text{Pd}_2\text{I}_6^{2-}$ the following rate law is obtained (II eq. 29):

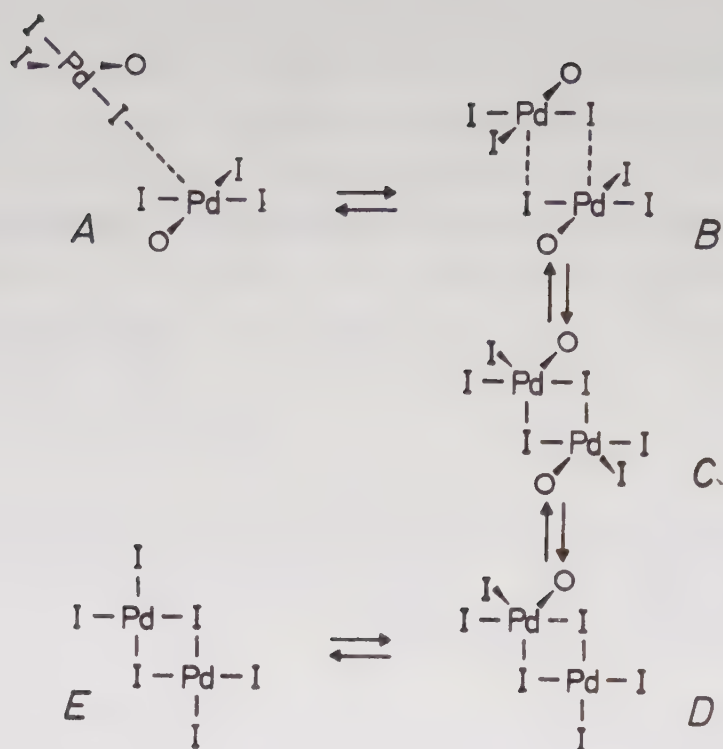


Fig. 3.1 Possible reaction mechanism for formation/dissociation of $\text{Pd}_2\text{I}_6^{2-}$. O denotes leaving/entering ligand, i.e. H_2O or I^- .

$$\begin{aligned} \text{RATE} = & (k_1 + k_2 K_4^{-1} [\text{I}^-]^{-1} + k_3 K_4^{-2} [\text{I}^-]^{-2}) [\text{PdI}_4^{2-}] \\ & - (k_{-3} + k_{-2} [\text{I}^-] + k_{-1} [\text{I}^-]^2) [\text{Pd}_2\text{I}_6^{2-}] \end{aligned} \quad (3.3)$$

(The notations are explained in II, eqns. (4) and (26)-(28)).

The concerted process proposed in paper II is not unambiguous because it is also possible to derive eq. (3.3) from a two-step mechanism involving a singly bridged intermediate formed in a rapid preequilibrium according to reaction (3.4):

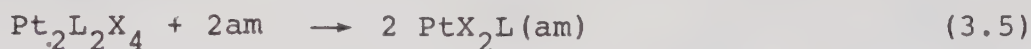


($\text{Y} = \text{H}_2\text{O}$ or I^- , $\text{M} = \text{Pd}^{2+}$, ionic charges omitted).

On the other hand, the second-order dependence on the

entering ligand is not compatible with a slow cleavage of the first bridge followed by a rapid cleavage of the second one - cf. II eq. (31) and the discussion on p. 2794.

It is obviously not possible from the kinetic measurements in II to decide which of these two mechanisms is the most plausible. However, product analysis of a number of analogous bridge-cleavage reactions according to eq. (3.5) may give further information.



X = Cl, Br or I, am = monodentate amine.

The halide-bridged platinum complex has the structure shown in Fig. 3.2. The bridge may be cleaved symmetrically as in Fig. 3.2 or unsymmetrically as in Fig. 3.3.

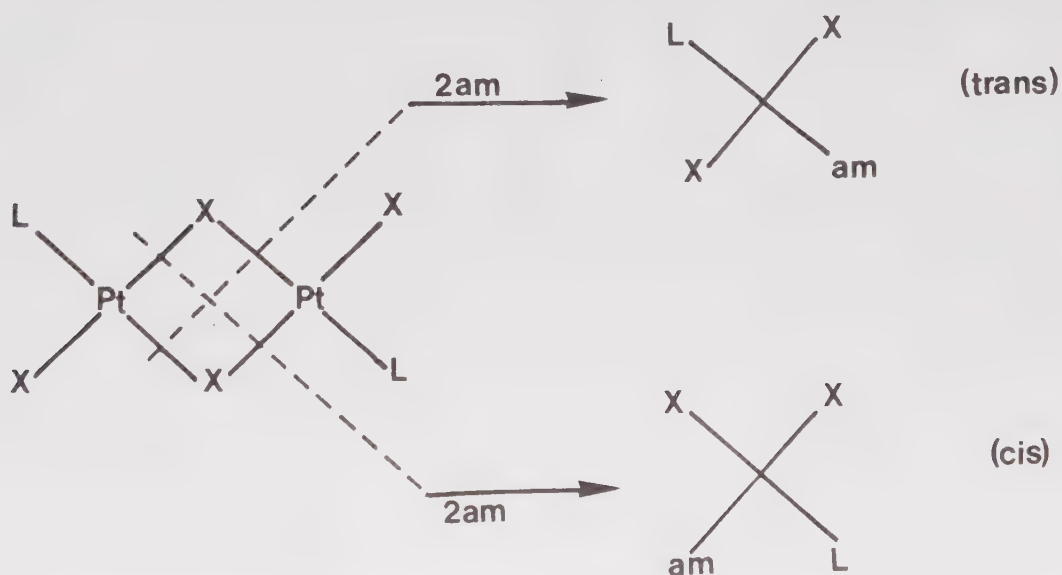


Fig. 3.2 Symmetrical cleavage.

Symmetrical cleavage, i.e. the attack by the two incoming ligands on different metal atoms in the complex is compatible with both mechanisms. According to mechanism (3.4), however, the two incoming ligands can also attack the same metal atom (cf. Fig. 3.3), which gives rise to unsymmetrical cleavage:

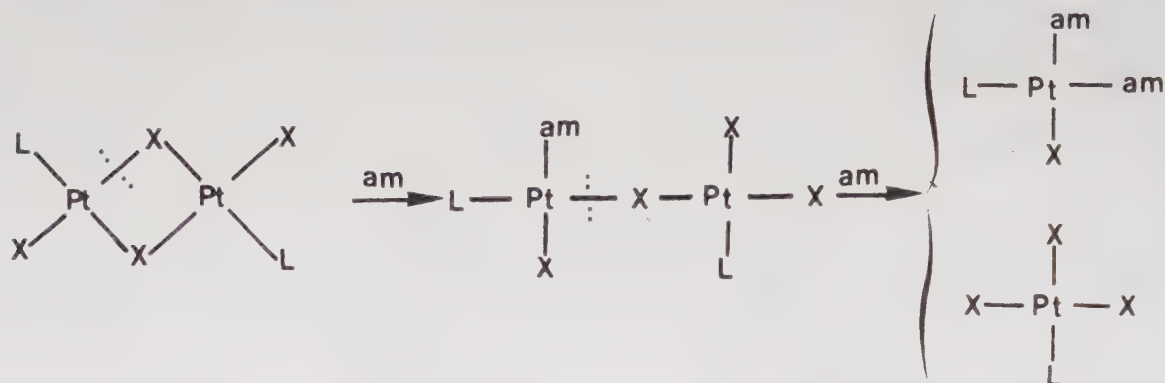


Fig. 3.3 Unsymmetrical cleavage. The dots indicate the bond cleaved in each stage.

Chatt and Venanzi⁹, Pearson, Muir¹⁰ and Cancio¹¹ have studied about 50 reactions of the type (3.5). In none of these did the product analysis give any evidence for unsymmetrical cleavage. This may be explained by assuming fast subsequent reactions of the products to those corresponding to symmetrical cleavage. However, this is unlikely. It is well-known that a substitution of an amine ligand in a platinum(II) complex such as $\text{cis-PtLX}(\text{am})_2$ is a slow process and therefore the presence of this species should have been revealed in a product analysis.

The simplest explanation is that with monodentate ligands and monoatomic bridging groups only symmetrical cleavage occurs. This supports the reaction model proposed in II with an activated complex which has the incoming ligands weakly bonded one to each of the metal atoms.

3.2. The redox reaction

In paper III the kinetics and mechanism for the reduction of tetrachloroaurate(III) by iodide is studied. The preferred mechanism is an outer-sphere redox reaction described as an attack by an iodide on one of the chloride ligands followed by an electron transfer to the central metal atom. (Alternative mechanisms will be discussed in conjunction with symmetry, cf. Chapter 6). The halogen molecule formed (ICl) leaves the complex and the linear dichloroaurate(I) complex may - in the presence of excess iodide - undergo substitution reactions to iodo-aurate(I)-complexes.

There are some peculiar features of this redox reaction. The reaction takes place in two steps when gold(III)-complex is in excess over iodide. An initial fast reduction by iodide with a simultaneous formation of diiodochloride is followed by a slower reduction of gold(III), either by diiodochloride or by iodide formed in a rapid pre-equilibrium between diiodochloride and chloride.

The experiments described in paper III disprove the interpretation by Hall and Satchell¹² of the reaction between tetrachloroaurate(III) and iodide as a substitution with a long-lived five-coordinated complex involved. The reaction they observed was most probably identical with the slow reduction process involving diiodochloride discussed above.

4. ABSORPTION SPECTRA AND SPECTRAL ASSIGNMENTS

4.1. Introduction

In IV, spectral assignments are proposed for both the d-d and the high-intensity bands of the chloro and bromo aqua complexes of platinum(II) and palladium(II). It is shown that the high-intensity bands are probably due to ligand p to metal d charge-transfer transitions in the palladium-halide complexes, whereas in

the platinum complexes they are better described as transitions from metal d to a mixture of metal and ligand p-orbitals. In this respect the halide complexes of gold(III) are probably analogous to those of palladium(II) (cf. ref. 13).

This difference between platinum and palladium complexes can be interpreted in terms of different relative energies of the molecular orbitals. These are discussed in Appendix 2. It is illustrated by the energy level diagrams in Fig. 4.1.

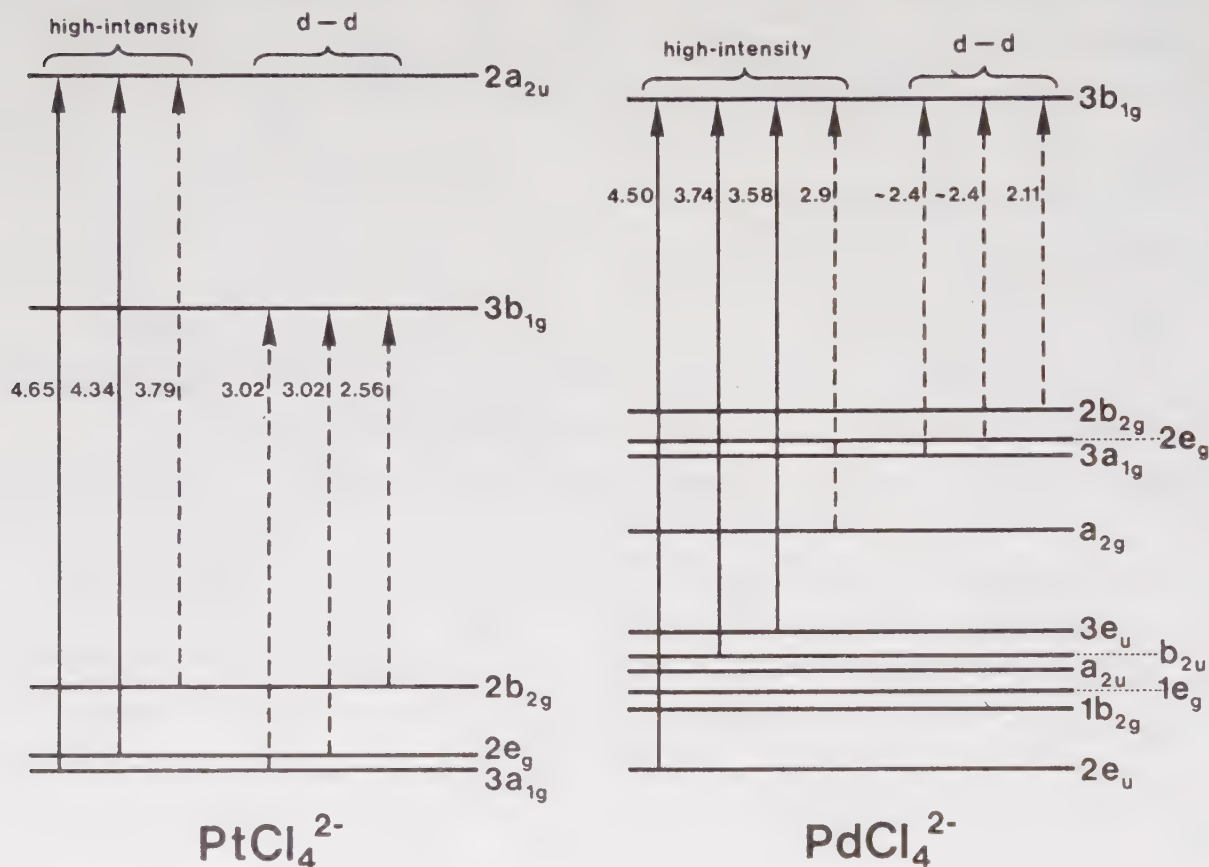


Fig 4.1 Suggested simplified energy level diagrams for PtCl_4^{2-} and PdCl_4^{2-} complexes in aqueous solution. Notation of energy levels according to ref. 14. The experimental wavenumbers in μm^{-1} have been included. Symmetry-forbidden transitions have been marked with dashed arrows and allowed transitions with full-drawn arrows. The diagram for PtCl_4^{2-} should be applicable for PtBr_4^{2-} also, and that for PdCl_4^{2-} for PdBr_4^{2-} . $1 \mu\text{m}^{-1} = 10 \text{ kK} = 1.24 \text{ eV} = 119.6 \text{ kJ mol}^{-1} = 4.56 \cdot 10^{-2} \text{ a.u.}$ A more complete energy level diagram is shown in Fig. 4.2.

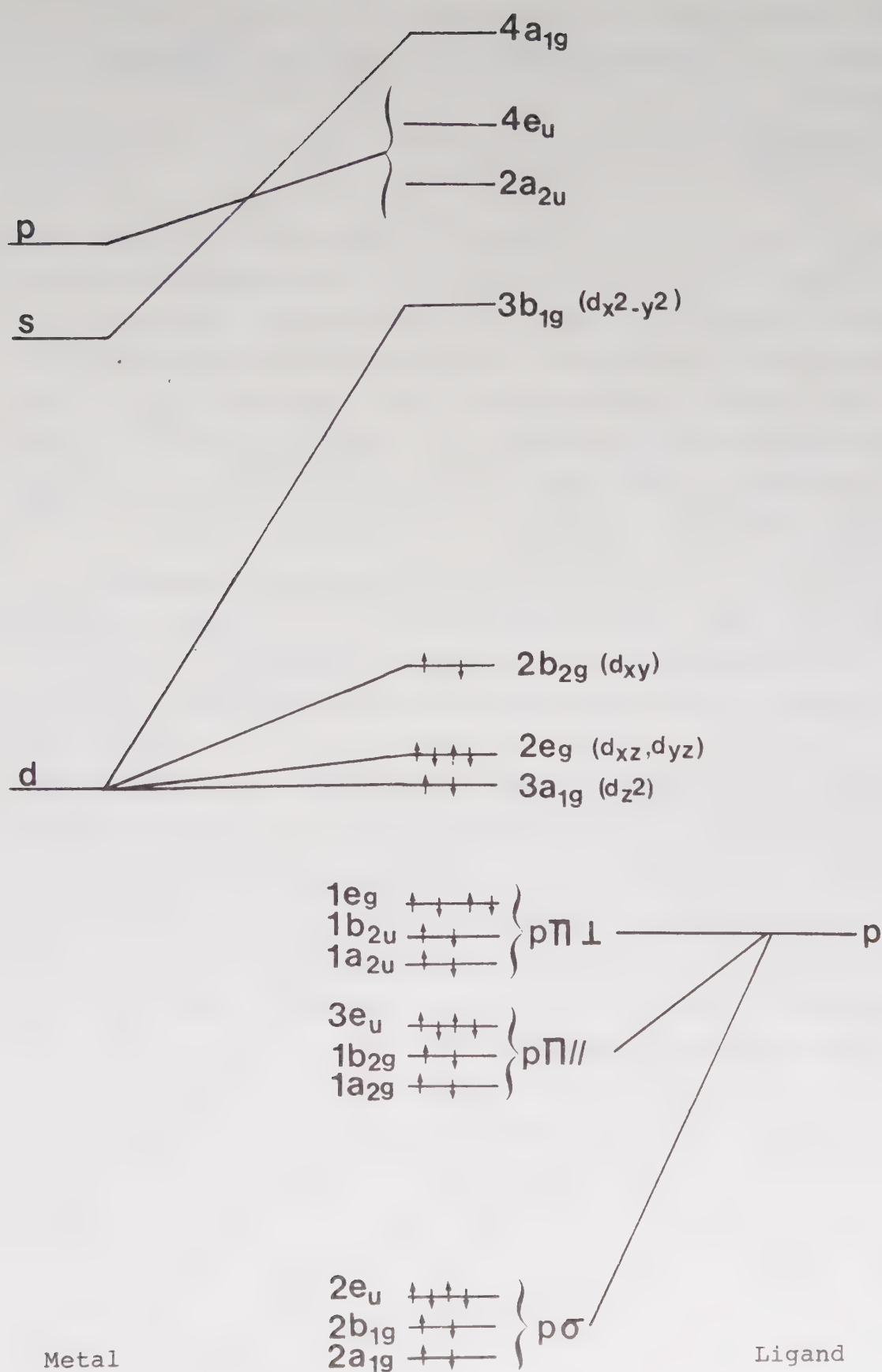


Fig. 4.2 One-electron molecular orbital energy levels (schematic). For notations see Appendix 2.

$3b_{1g}$ (which can be described as mainly metal d) has a higher energy relative to the $2e_u$ and $3e_u$ levels (mainly ligand p) in the platinum complexes than in those of palladium. Conversely, $2a_{2u}$ (metal and ligand p) has a lower energy relative to the metal d ($2b_{2g}$, $2e_g$ and $3a_{1g}$) levels in the platinum complexes.

These differences are important for the description of mechanisms for substitution and redox reactions in terms of orbitals and their energies and symmetry. The reason is that the most intense bands in palladium and gold complexes are probably due to transitions from σ -bonding ($2e_u$) to σ -antibonding ($3b_{1g}$) orbitals (cf. Appendix 2), which are essential orbitals for the description of σ -bond-breaking in a chemical reaction. In the platinum complexes, on the other hand, all the observed high-intensity bands are due to transitions from non-bonding (or weakly anti-bonding) d-orbitals ($2b_{2g}$, $2e_g$ and $3a_{1g}$) to a π -antibonding orbital ($2a_{2u}$), all of which are unimportant as far as σ -bond-breaking is concerned.

The energy difference between $2e_u$ and $3b_{1g}$ is expected to be larger in $PtCl_4^{2-}$ than in $PdCl_4^{2-}$, and an estimate is given in 4.2. Consistent with this, the breaking of σ -bonds requires more energy in the platinum complexes than in those of palladium. This fact is also relevant for the observed differences in reactivity of about five or six orders of magnitude between the platinum complexes and those of palladium and gold, see Chapter 6.

It is thus essential to analyze carefully the experimental basis for the proposed assignments. This is done in IV for the chloro and bromo aqua complexes. The spectra of PdI_4^{2-} , $Pd_2I_6^{2-}$ and PtI_4^{2-} reported in II (Fig. 1c) and in Appendix 1 give additional information. Band maxima and molar absorptivities for the high-intensity bands are summarized in Table A 1 in Appendix 1 for the six complexes PdX_4^{2-} and PtX_4^{2-} , X = Cl, Br and I. The values for PtI_4^{2-} are in

agreement with the spectrum reported by Corain and Poë.¹⁵

4.2. Assignments for the high-intensity bands

The spectral assignments for the bands of PtCl_4^{2-} and PdCl_4^{2-} proposed in IV were based mainly on polarized crystal spectra of the potassium salts of tetrachloroplatinate(II) and -palladate(II) and on solution spectra of the series of mixed chloro aqua complexes. In order to use both sets of data it is necessary to assume that the coordination geometry of the anionic complexes PtCl_4^{2-} and PdCl_4^{2-} is the same in the solid state^{16,17} as in solution. This is reasonable, since, as shown in IV Tables IV and V, both band positions and molar absorptivities for crystal and solution spectra are very similar both for the d-d and the high-intensity bands.

We can now include the iodo complexes into the comparison between the spectral changes for the two series of complexes, $\text{PtX}_4^{2-}(\text{aq})$ and $\text{PdX}_4^{2-}(\text{aq})$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$, see Table A 1 in Appendix 1. For the symmetry allowed bands we find that there are shoulders at the low energy sides of the bands of PdBr_4^{2-} . These were assigned singlet-triplet transitions, cf. IV p. 73. The theoretical explanation is given by the so-called spin-orbit effect, which, if large, invalidates the spin-selection rule.¹⁸ The effect increases with atomic number. Accordingly, the two high-intensity bands in $\text{PdCl}_4^{2-}(\text{aq})$ (4.50 and $3.58 \mu\text{m}^{-1}$) correspond to two intense bands (4.06 and $3.04 \mu\text{m}^{-1}$) each accompanied by a weak shoulder (3.73 and $2.74 \mu\text{m}^{-1}$) in PdBr_4^{2-} and to four intense bands in PdI_4^{2-} , two of which are assigned singlet-singlet-transitions (3.75 and $2.47 \mu\text{m}^{-1}$) and the other two singlet-triplet transitions (3.19 and $2.03 \mu\text{m}^{-1}$). (This interpretation for the pair of bands $2.47, 2.03 \mu\text{m}^{-1}$ seems to have been first suggested by Jørgensen, ref. 19 Table XXIV). Another possibility is to assign the band at $3.19 \mu\text{m}^{-1}$ (315 nm) to a singlet-singlet transition (${}^1\text{E}_{\text{u}1} \leftarrow {}^1\text{A}_{1\text{g}}$) with the corresponding singlet-triplet at $2.47 \mu\text{m}^{-1}$ (407 nm), but this is less plausible, cf. 4.3.

The situation is quite different for the corresponding Pt(II)-complexes. The two adjacent bands around $4.5 \mu\text{m}^{-1}$ in the PtCl_4^{2-} -spectrum are also displaced towards the visible when chloride is substituted by bromide, cf. Elding and Gröning, ref. 20 Fig. 2 and Table X, but, as remarked by these authors,^{20, p 14} no new shoulders at the low-energy side are seen in the spectrum of PtBr_4^{2-} , nor in that of PtI_4^{2-} , cf. Appendix 1, Table A 1. The energy difference between the two high-intensity bands is $0.3 \mu\text{m}^{-1}$ in PtCl_4^{2-} and PtBr_4^{2-} and $0.4 \mu\text{m}^{-1}$ in PtI_4^{2-} . The splittings in the palladium(II)-complexes between the suggested singlet-singlet- and singlet-triplet-transitions are $0.3 \mu\text{m}^{-1}$ in PdBr_4^{2-} and $0.5 \mu\text{m}^{-1}$ in PdI_4^{2-} . It is encouraging to compare these values with the analogously explained splitting in the spectra of the isoelectronic noble gases $\text{Kr}(\text{Br}^-)$ and $\text{Xe}(\text{I}^-)$. It is $0.51 \mu\text{m}^{-1}$ in the former and nearly twice as large, $0.91 \mu\text{m}^{-1}$, in the latter, cf. ref. 19 p. 268f and Table I. (Consistently with this the splitting is small for $\text{Ar}(\text{Cl}^-)$, only $0.15 \mu\text{m}^{-1}$. No shoulders are observed in PdCl_4^{2-} !).

For PtBr_4^{2-} and PtI_4^{2-} there is a high-intensity band at 4.63 and $3.78 \mu\text{m}^{-1}$ respectively, which has not been assigned so far. It is so intense that it must necessarily arise from a symmetry allowed and (at least in PtBr_4^{2-}) a spin-allowed transition. Therefore ${}^3\text{E}_u \leftarrow {}^1\text{A}_{1g}$ ($3b_{1g} \leftarrow 3e_u$) seems unlikely. It is also less probably due to the corresponding singlet-singlet-transition, since there is no shoulder at the low-energy side of the band (cf. PdBr_4^{2-} above). Another possibility which might be discarded is ${}^1\text{E}_u \leftarrow {}^1\text{A}_{1g}$ ($2a_{2u} \leftarrow 1e_g$). From Fig. 4.1 it follows that the $2a_{2u}$ -level lies far above $3b_{1g}$ whereas $1e_g$ has approximately the same energy as $3e_u$. Accordingly, the suggested transition should have a higher energy than ${}^1\text{E}_u \leftarrow {}^1\text{A}_{1g}$ ($3b_{1g} \leftarrow 3e_u$).

A more reasonable suggestion for the assignment of these two bands in PtBr_4^{2-} and PtI_4^{2-} is $4e_u \leftarrow 2b_{2g}$ (cf. Fig. 4.2). One problem is that the position of the

$4e_u$ -level is unknown. However, in the LCAO-approximation (cf. Appendix 2) $4e_u$ can be described as composed of the Pt p(in-plane)- and ligand $p\pi||$ -orbitals and should therefore be expected to lie rather near to the $2a_{2u}$ -level, which is also composed of p-orbitals - Pt p_z (out-of-plane) and ligand $p\pi\perp$ (see Appendix 2). This implies that the change of the transition $2a_{2u} \leftarrow 2b_{2g}$ between PtBr_4^{2-} and PtI_4^{2-} should be nearly the same as that for $4e_u \leftarrow 2b_{2g}$. This agrees with experiments. The $2a_{2u} \leftarrow 2b_{2g}$ band changes from $3.18 \mu\text{m}^{-1}$ (PtBr_4^{2-}) to $2.32 \mu\text{m}^{-1}$ (PtI_4^{2-}) i.e. $0.86 \mu\text{m}^{-1}$ and the change for the unassigned band is exactly the same, viz. $0.85 \mu\text{m}^{-1}$ (4.63 to $3.78 \mu\text{m}^{-1}$).

The assignments for these bands have some importance for the following mechanistic discussion (cf. Chapter 6). If $4e_u \leftarrow 2b_{2g}$ is correct this implies that the $2e_u$ -level must be very low in energy. From the transition energy of the $4e_u \leftarrow 2b_{2g}$ -band in PtBr_4^{2-} ($4.63 \mu\text{m}^{-1}$ or 216 nm) it follows that the $3b_{1g} \leftarrow 3e_u$ -band must lie below 200 nm i.e. the transition energy must be higher than $5.0 \mu\text{m}^{-1}$. If we assume that the difference between $3e_u$ and $2e_u$ is similar in this complex and PdBr_4^{2-} (cf. Appendix 1, Table A 1), the transition energy of ${}^1E_u \leftarrow {}^1A_{1g}$ ($3b_{1g} \leftarrow 2e_u$) should be at least $6 \mu\text{m}^{-1}$. A comparison between PdCl_4^{2-} and PdBr_4^{2-} concerning this transition (cf. Appendix 1, Table A 1) shows that it is $0.4 \mu\text{m}^{-1}$ higher in the former complex. If this is true for PtCl_4^{2-} also, the transition energy should be at least $6.4 \mu\text{m}^{-1}$ (160 nm). The essential conclusion from this discussion is that no bands of PtCl_4^{2-} between 190 and 200 nm (5.3 to $5.0 \mu\text{m}^{-1}$) can be due to $3b_{1g} \leftarrow 2e_u$. The energy of this transition must be considerably higher for PtCl_4^{2-} than for PdCl_4^{2-} , where it is $4.50 \mu\text{m}^{-1}$.

4.3. Position of the d-levels

The proposed assignments for the high-intensity bands in the PdCl_4^{2-} and PtCl_4^{2-} -spectra imply that the positions of the d-levels are different for the palladium and platinum complexes. In PtCl_4^{2-} the d-orbitals have a higher energy and

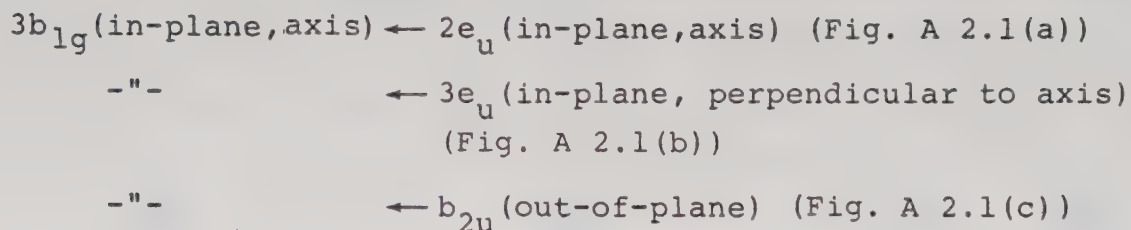
are more extended in space than in PdCl_4^{2-} . The same is valid for the neutral free metal atoms, which is shown by the spectra of the gaseous atoms (cf. ref. 21 p. 4415). A calculation²² by a relativistic extended Hückel method²³ on PdCl_4^{2-} and PtCl_4^{2-} shows that the orbital energies for the valence d-orbitals are higher by 1.1 to 1.5 μm^{-1} for the latter complex. In the quantum-mechanical calculations the inclusion of a spin-orbit term in addition to the electron repulsion term ($1/r_{ij}$) is considerably more important for platinum than for palladium (cf. page 16). When this and other relativistic terms are important, the shape of the orbitals is affected so the d-orbitals are more extended and the s- and p-orbitals more contracted than when these terms are negligible. This is obviously in conformity with the assignments; the difference in energy between 5d(Pt)-, 4d(Pd)-orbitals ($2e_g$, $3a_{1g}$, $2b_{2g}$, $3b_{1g}$) and the empty 6p(Pt)-, 5p(Pd)-orbitals ($2a_{2u}$, $4e_u$) is lower in platinum(II) than in palladium(II) complexes.

The electronic differences between the complexes have chemical consequences. The d-electrons are involved in redox processes; the oxidation number II has d^8 -configuration and IV has d^6 . The ease of oxidation is related to the accessibility of two of the metal d-electrons for an oxidant. Consequently we can expect that oxidation from II to IV is more favourable for platinum complexes than for those of palladium.

4.4. Molar absorptivities for the high-intensity bands of PdX_4^{2-} and PtX_6^{2-}

Theoretically, the absorptivity due to a transition between an initial energy level (with a corresponding orbital φ_i) and a final level (with φ_f) is proportional to an integral $\langle \varphi_i | \bar{P} | \varphi_f \rangle$ ($= \int \varphi_i \bar{P} \varphi_f d\tau$), where $\bar{P}$ is the dipole operator. This integral may be equal to zero by symmetry arguments or when φ_i and φ_f are localized in different regions of space.

The relevant molecular orbitals involved in the transitions of PdX_4^{2-} are (cf. Appendix 2)



where axis denotes the ligand-metal axis. According to the LCAO-description shown in Appendix 2, Fig. A 2.1, the in-plane $3b_{1g}$, $2e_u$ and $3e_u$ -orbitals extend over the whole complex. This is not so for b_{2u} , because it has no metal atomic-orbital component. Moreover, the intensity from a transition, where the filled orbital is doubly degenerate, will be favoured by a factor of 2 as compared to when it is non-degenerate. In summary, this fact and the indicated extension in space of the orbitals leads to the conclusion that the molar absorptivity should vary in the following way:

$$\epsilon(3b_{1g} \leftarrow 2e_u) > \epsilon(3b_{1g} \leftarrow 3e_u) \gg \epsilon(3b_{1g} \leftarrow b_{2u}).$$

This is in agreement with experiments (cf. IV Table V, $\text{K}_2\text{PdCl}_4(\text{s})$); the values are $2.76 \cdot 10^4$, $1.4 \cdot 10^4$ and $3.88 \cdot 10^2 \text{ cm}^{-1} \text{ M}^{-1}$, respectively.

It is possible to rationalize the transitions in $\text{Pd}_2\text{X}_6^{2-}$, using the same assignment as in PdX_4^{2-} , because the arrangement of the halide ligands around each palladium atom is very nearly equal to that in the monomer (cf. ref. 24 for bond lengths and angles in $\text{Pd}_2\text{Br}_6^{2-}$) and since the oxidation number is the same. As far as the orbitals are concerned it should be expected that the empty molecular orbitals $3b_{1g}(\text{d}_{x^2-y^2})$ of the two palladium atoms and the filled $2e_u$ (ligand $p\sigma$) and $3e_u$ (ligand $p\pi||$) of the four terminal halide ligands are only slightly affected. However, the two bridging ligands must use both of the two sets of in-plane p-orbitals (denoted $p\sigma$ and $p\pi||$ in Appendix 2)

for σ -bonding, one set to each of the two palladium atoms. Accordingly, the bridging-ligand p-components will give only a minor contribution to the orbitals denoted $1a_{2g}$ ($p\pi||$), $1b_{2g}$ ($p\pi||$) and $3e_u$ ($p\pi||$) in PdX_4^{2-} .

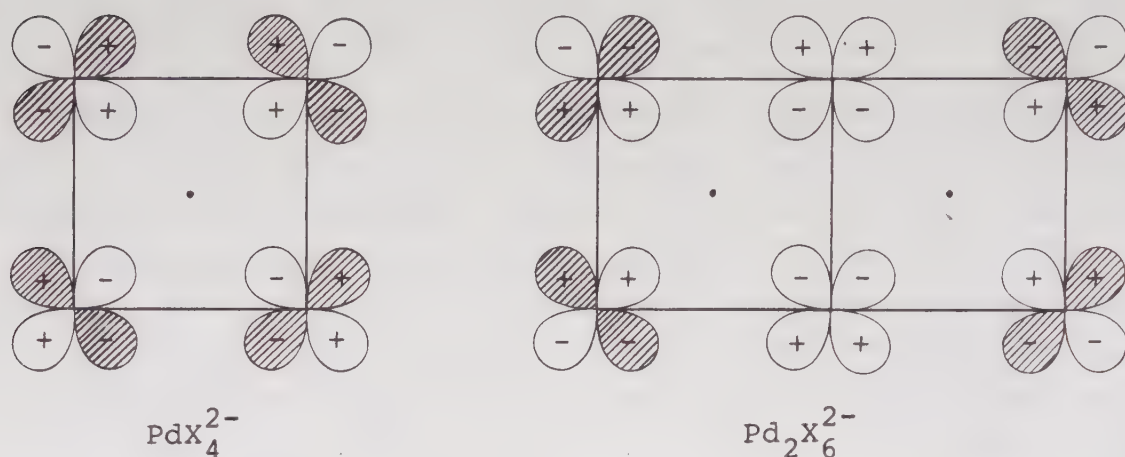


Fig. 4.3 Ligand $p\pi||$ (hatched) and $p\sigma$ orbitals of PdX_4^{2-} and $Pd_2X_6^{2-}$. Note that the p-orbitals of the bridging ligands are directed towards the Pd atoms. Schematically they can thus be classified as $p\sigma$ -orbitals, cf. Appendix 2.

Consequently, $Pd_2X_6^{2-}$ should have a band corresponding to the band of PdX_4^{2-} described as $3b_{1g} (d_{x^2-y^2}) \leftarrow 2e_u(p\sigma)$ with a nearly equal transition energy. Its molar absorptivity should be expected to be twice as large in $Pd_2X_6^{2-}$ as compared to PdX_4^{2-} , because the number of absorbing units per mole is doubled. Therefore we can identify the band at $3.19 \mu m^{-1}$ (314 nm) in PdI_4^{2-} with that at $3.00 \mu m^{-1}$ (333 nm) in $Pd_2I_6^{2-}$, cf. II Fig. 1c. The molar absorptivity has increased from $1.7 \cdot 10^4$ to $4.8 \cdot 10^4 \text{ cm}^{-1} \text{ M}^{-1}$.

On the other hand, the molar absorptivity for the band assigned $3b_{1g} \leftarrow 3e_u (p\pi||)$ in PdX_4^{2-} should not change. This band has a transition energy of $2.47 \mu m^{-1}$ (405 nm) and a molar absorptivity of $10^4 \text{ cm}^{-1} \text{ M}^{-1}$ in PdI_4^{2-} . Unfortunately, it is difficult to resolve the visible tail of the band of

$\text{Pd}_2\text{I}_6^{2-}$ at 333 nm (cf. II Fig. 1c) into single bands. It is obvious that there are bands in this region of the spectrum with roughly the expected molar absorptivity.

The most essential conclusion from this discussion is that the two bands of PdI_4^{2-} cannot be assigned as singlet-singlet ($3.19 \mu\text{m}^{-1}$) and its accompanying singlet-triplet ($2.47 \mu\text{m}^{-1}$) transition.

4.4. The electronic terms for PdX_4^{2-} and PtX_4^{2-}

The terms with known energy arising from different electron configurations are shown in Fig. 4.4 (a) (PdX_4^{2-}) and 4.4 (b) (PtX_4^{2-}), respectively, with the ground-state configuration (which gives the $^1\text{A}_{1g}$ term) as zero point. For the chloride complexes, the configurations corresponding to the different terms have been displayed, as have the terms corresponding to the d-d-transitions. The singlet-triplet d-d-bands of PtCl_4^{2-} have been assigned according to Martin et.al. cf. IV Table IV. All the terms corresponding to d-d-transitions in PdCl_4^{2-} have been given the same energy; a very small splitting is known to exist, cf. IV Table V. The same is also true for the $^1\text{E}_u$, $^1\text{A}_{2u}$ -terms in PdCl_4^{2-} and probably for PdBr_4^{2-} and PdI_4^{2-} also. It has been assumed that the $^3\text{A}_{2u}$ -term has the same energy as $^3\text{E}_u((3e_u)^3 3b_{1g})$. This is not shown by the spectra, because the band assigned $^3\text{A}_{2u} \leftarrow ^1\text{A}_{1g}$ ($3b_{1g} \leftarrow b_{2u}$) has a very low intensity. This can be inferred from the intensity ratio between the bands assigned $^1\text{E}_u \leftarrow ^1\text{A}_{1g}$ and $^3\text{E}_u \leftarrow ^1\text{A}_{1g}$, respectively and the known value ($388 \text{ cm}^{-1} \text{ M}^{-1}$) for $^1\text{A}_{2u} \leftarrow ^1\text{A}_{1g}$ (cf. also Herzberg ref. 18).

The term assigned $^3\text{B}_{2g}$ in PdI_4^{2-} is just a reasonable guess. As discussed earlier, it has not been possible to assign definitely the high energy band at 4.63 (PtBr_4^{2-}) and 3.78 (PtI_4^{2-}) μm^{-1} . The suggestion $4e_u \leftarrow 2b_{2g}$ (cf. page 17) implies an E_u -term.

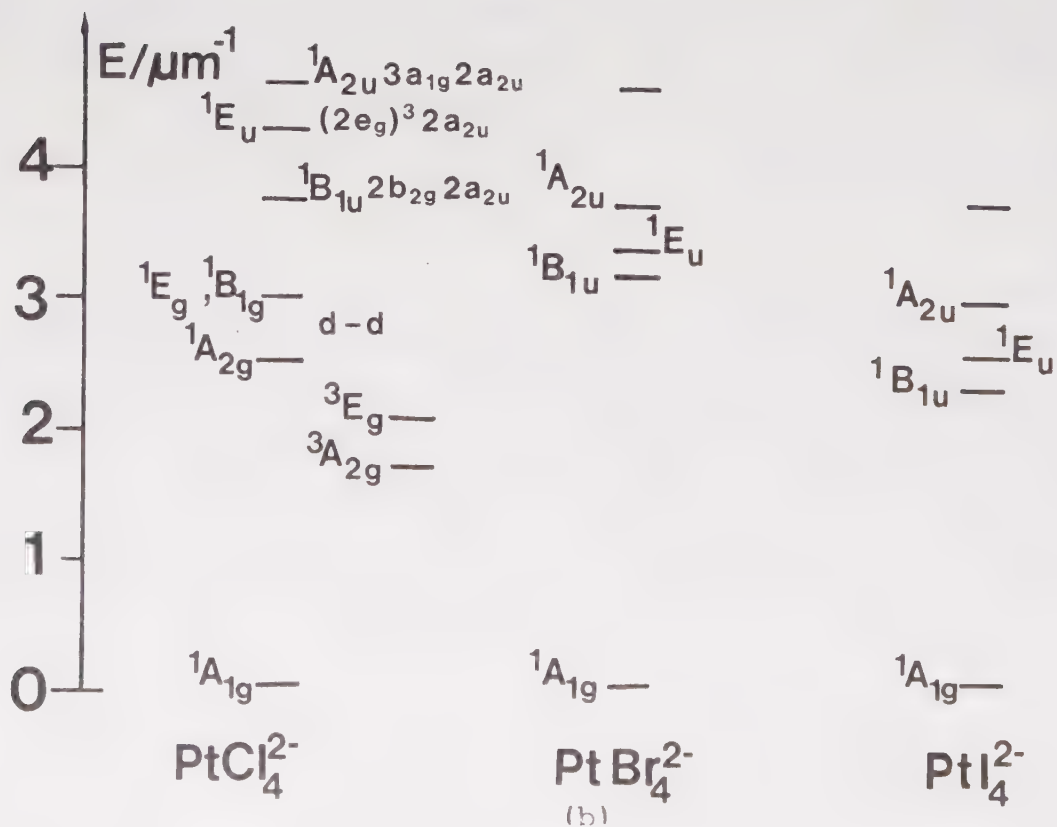
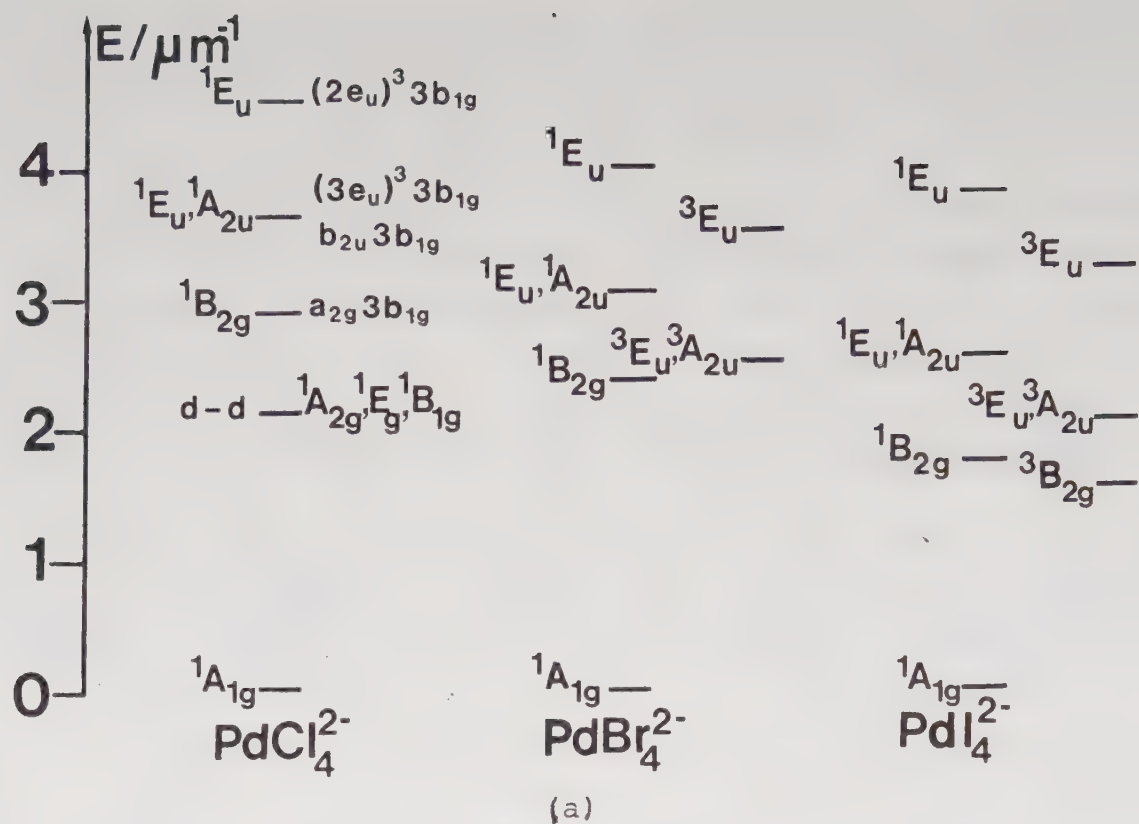


Fig. 4.4 Observed electronic states of PdX_4^{2-} (a) and PtX_4^{2-} (b); X = Cl, Br and I.

Finally, it should be remarked that the observed transitions in the palladium complexes, assigned $3b_{1g} \leftarrow 2e_u$ and so on, should occur also in the platinum complexes but at considerably higher energies (beyond the range of the spectrophotometer). Similarly, transitions observed in the platinum spectra, assigned $2a_{2u} \leftarrow 2e_g$ and so on, occur at considerably higher energies in those of palladium.

4.5. The assignments of the bands in AuX_4^- , $X = Cl$ and Br

According to Elding and Gröning²⁵ the high-intensity bands of AuX_4^- can be assigned as in PdX_4^{2-} , but not as in PtX_4^{2-} ($X = Cl, Br$). From the earlier discussion about the extension in space of the d-orbitals and the fact that platinum and gold have nearly equal atomic numbers the converse may seem more plausible (cf. the discussion of the spin-orbit effect on pages 16 and 19). However, the nuclear charge is one unit larger for gold than for platinum, whereas the number of electrons is the same. This means that the attractive electrostatic potential energy for the valence-d-electrons is higher for gold than for platinum. Correspondingly, the d-orbitals are closer to the nucleus in the former. Therefore, the transitions assigned $2a_{2u} \leftarrow (2b_{2g}, 3e_g, 3a_{1g})$ must occur at higher energies in $AuCl_4^-$ than in $PtCl_4^{2-}$. The observed transitions in the former complex have smaller energies than in the latter and the identical assignment with $PdCl_4^{2-}$ seems to be the most likely alternative.

5. AXIAL INTERACTIONS

The electronic structure of square-planar halide complexes is not favourable for additional bonding of a fifth or a sixth halide ligand. The complexes have one filled orbital of high energy in the axial direction i.e. $3a_{1g}$ (d_{z^2}). The incoming nucleophile has no low-energy empty orbitals, only filled ones. Among these it is always possible to choose one of correct symmetry. Thus both the bonding and anti-

bonding orbitals formed in the hypothetical addition of a fifth ligand above the plane are filled. No net bonds will be formed.

The species PdCl_5^{3-} or PdCl_6^{4-} are probably not present in moderately concentrated (1 M) chloride solutions of palladium(II), cf. II p. 2792 and ref. 4(a). The spectrum of chloropalladate(II) in 10 M hydrochloric acid solution²⁶ is very similar to that in 1 M chloride. Small changes²⁷ might be due to slight oxidation to palladium(IV) in the concentrated hydrochloric acid solutions. PdBr_6^{4-} has been proposed to exist in nitrobenzene,²⁸ but that proposal was based on the unlikely assumption that no mixed solvento-bromide-complexes existed in the absence of added free bromide (further more, it was found that only a compound containing PdBr_4^{2-} , but not PdBr_6^{4-} could be recovered even in the presence of free bromide). The same objection can be raised against another investigation²⁶ where the d-d-spectrum of PtCl_4^{2-} in 1, 2 and 10 M hydrochloric acid was reported. The result does not speak in favour of five- or six-coordination. The band assigned ${}^1\text{B}_{1g} \leftarrow {}^1\text{E}_g \leftarrow {}^1\text{A}_{1g} (d_{x^2-y^2} \leftarrow d_{z^2}, d_{xz}, d_{yz})$ is displaced towards shorter wavelengths. However, theoretically, the addition of a negative species above and below the plane should be expected to decrease the ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g} (d_{x^2-y^2} \leftarrow d_{z^2})$ transition energy, i.e. displace the band towards longer wavelengths (in the limiting case of a hypothetical octahedral PdCl_6^{4-} , $d_{x^2-y^2}$ and d_{z^2} are of equal energy).

It is noteworthy that the existence of nickel(II) complexes of both four-coordinated square-planar and six-coordinated octahedral geometry is in agreement with the arguments presented above. Square-planar nickel(II) complexes²⁹ have a low-spin (i.e. singlet) ground state term corresponding to the same d-electron configuration as that of square-planar palladium(II) and platinum(II) complexes i.e. $d_{xz}^2 d_{yz}^2 d_{xy}^2 d_{z^2}^2$. Regular octahedral nickel(II) complexes (ibid. p. 1154) have always a high-spin (triplet) ground-

state term. It corresponds to the d-electron configuration $d_{xz}^2 d_{yz}^2 d_{xy}^2 d_{z^2}^1 d_{x^2-y^2}^1$ (with two unpaired electrons) i.e. the electronic charge in the axial direction (given by d_{z^2}) is reduced and the spin state is a triplet. Thus, one spin orbital is empty. In nickel(II) complexes the energy difference between the filled and empty d-orbitals is so small that the energy gained by spin-pairing is comparable to the energy gained by axial bond formation. This choice seems not to exist for palladium(II) and platinum(II) complexes.

The electronic factors which disfavour five- and six-coordination are also relevant for a mechanistic discussion. A perpendicular approach of an incoming nucleophile in square-planar substitution reactions is obviously energetically unfavourable.

In other mechanisms the presence of a five-coordinated platinum complex has been assumed. For example, Basolo, Pearson and coworkers³⁰ assumed the active participation of $PtCl_5^{3-}$ in substitution reactions of platinum(IV)-complexes, which are influenced by the presence of platinum(II)-complexes. Elding and Gustafson³¹ showed, however, that only a four-coordinated complex had to be invoked.

In summary, neither spectrophotometric equilibrium measurements nor indirect evidence from kinetic measurements speak in favour of palladium(II) and platinum(II) halide complexes with coordination number higher than four.

It should be remarked that the presence of the filled $3a_{1g}$ (d_{z^2})-orbital which makes coordination of halide in the axial position unfavourable, on the other hand facilitates oxidation by a free halogen molecule. Such species have an empty orbital of low energy (σ_u) and of correct symmetry to accept electrons.

6. ORBITAL SYMMETRY AND REACTION MECHANISMS

6.1 Introduction

The mechanisms described in Chapter 3 were deduced from rate laws. In the present chapter they will be discussed in relation to the symmetry of the possible internal motions of the complex (molecular vibrations, cf. Fig. 6.1) and the electronic state wave-functions and their corresponding orbitals. The symmetry and energy eigenvalues of the state wave-functions can be found in Fig. 4.4, which also contains the relevant orbitals. The symmetry properties of the latter are displayed in Appendix 2 Fig. A 2.1.

In principle, the motions of the atoms in the complex and the incoming ligand should be considered. In the simpler and more useful approach employed here the internal motions of the complex will first be considered and one motion selected as a plausible reaction path. Then the different reactivity of PtX_4^{2-} and PdX_4^{2-} and the trend in reactivity for the latter complex in the series $\text{X} = \text{Cl}, \text{Br}$ and I will be discussed. Finally, the π - and σ -trans effects will be introduced via the concept "transition density". This will suggest both a reaction mechanism for reductive elimination and favourable paths for an incoming ligand in a substitution process.

Pearson⁶ has discussed both substitution reactions, cf. ref. 6 p. 187f, 268 and 316, and redox reactions p. 286, 405f. He makes use of the mechanism suggested by Chatt et. al.³² and elaborated by Langford and Gray,³³ involving an attack by the incoming ligand above the plane. Pearson also shows that there are two possible mechanisms for reduction which both are symmetry allowed, one inter- and one intramolecular path, respectively. One of them can be shown to be a special case of the σ -trans effect.

In any comparison between theory and experiments it must be

born in mind that there are properties which are not symmetry related, but which can influence the rate. One example is the ionic charge of the complex.

6.2. Selection of orbitals, motions and states in the D_{4h} -complexes

The symmetry species of the possible motions (shown in Fig. 6.1) are A_{1g} , B_{1g} , B_{2g} , A_{2u} , B_{2u} and the two E_u :s. If the complex is not exposed to external influence, the motions all occur as normal vibrations of the ground-state complex i.e. with small amplitudes. In the initial stage of a chemical reaction a suitable motion is activated by interaction with the incoming ligand. With the monoatomic entering ligands considered here, the activation is determined mainly by the intrinsic properties of the complex.

The energy change due to a displacement of the atoms in the complex can be described by a polynomial in the symmetry adapted displacement coordinates Q , one for each motion in Fig. 6.1. There are terms corresponding both to energy increase and decrease. The energy decrease for a motion is given by expression (6.1) (cf. ref. 6, p. 13)

$$\left(\sum_{k=1}^{\infty} \frac{\langle \psi_0 | \partial U / \partial Q | \psi_k \rangle^2}{E_k - E_0} \right) Q^2 \quad (6.1)$$

(only one motion is considered). E_0 is the energy at $Q = 0$ (the ground-state configuration), ψ_0 is the electronic ground-state wave-function and ψ_k ($k > 0$) denotes the wave-functions of the excited states with eigenvalues E_k ($> E_0$). U is the electrostatic potential energy. Classically, $\partial U / \partial Q$ is the electrostatic force along the Q -coordinate. It has thus the same symmetry species as Q or, in other words, the arrows in Fig. 6.1 also represent the forces acting on the nuclei.

A large value of the sum in (6.1) means that the necessary energy for a distortion of the complex along the Q -mode

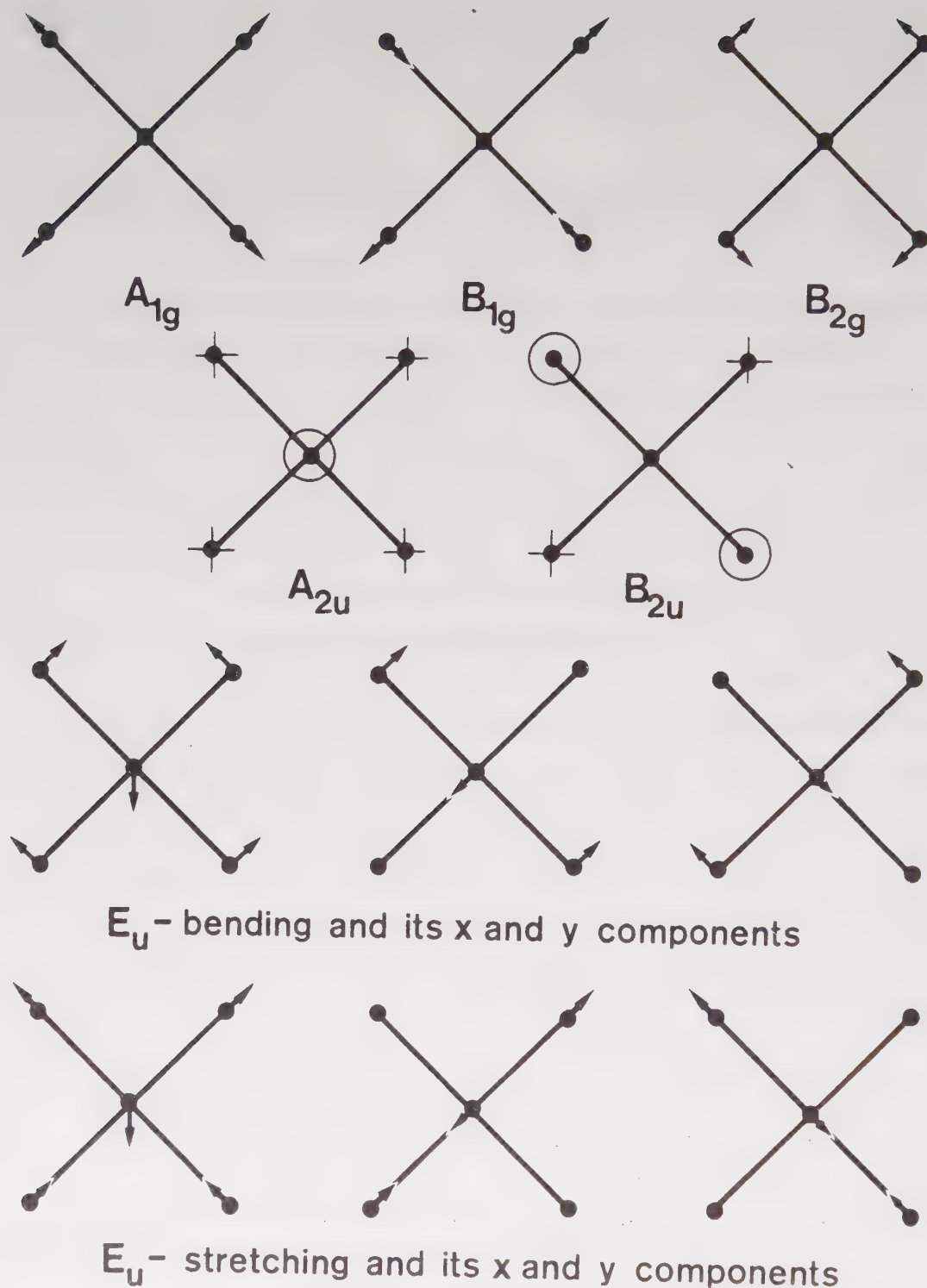


Fig. 6.1 Vibrational modes for MX_4 (D_{4h}) compounds. Circles and crosses denote antiparallel out-of-plane motion.

is small or even negative. Its magnitude depends upon the presence of accessible (i.e. small $E_k - E_0$) excited states of correct symmetry. The latter requires that the integrand $\psi_0 (\partial U / \partial Q) \psi_k$ must be totally symmetric i.e. the product $\psi_0 \psi_k$ must be of the same symmetry species as the motion Q . This product is called the transition density and is denoted ρ_{ok} , i.e. $\rho_{ok} = \psi_0 \psi_k$. The change of the electron density is to first order given by the expression (6.2)

$$\frac{1}{2} \frac{\langle \psi_0 | \partial U / \partial Q | \psi_k \rangle}{E_k - E_0} \rho_{ok} \quad (6.2)$$

cf. ref. 6, p. 24.

The energy requirement, $E_k - E_0$, is easy to estimate quantitatively from the term schemes in Fig. 4.4. The numerators in (6.1) are harder to assess, but at least a qualitative estimate can be made if the state wave-functions are replaced by their proper molecular orbitals (cf. Fig. 4.4). Expressed in this way there must be low-energy unoccupied molecular orbitals (LUMO) present which can interact with high-energy occupied molecular orbitals (HOMO). The symmetry species of the product of one HOMO and one LUMO must be the same as one of the motions in Fig. 6.1. This product is the transition density expressed by molecular orbitals and can be visualized as an electron flow from the filled orbital (HOMO) to the empty one (LUMO). It may correspond to bond changes during the reaction (and in extreme cases even to reduction). The numerator in (6.1) will be large if the orbitals are localized in the same region of space (the discussion will be similar to the one about molar absorptivities in section 4.4) and if ρ_{ok} correspond to large changes in the electron density around the moving atoms (cf. ref. 34). So, for instance, the motion denoted B_{1g} in Fig. 6.1 is a pure ligand motion. The orbitals with lowest energy difference, which - for reasons of symmetry - may decrease the B_{1g} -activation energy are $3a_{1g}(d_z^2)$ (HOMO) and $3b_{1g}(d_{x^2-y^2})$ (LUMO). These

are, however, of metal-d-character i.e. they will mainly change the electron density around the central metal atom. Accordingly, the force acting on the ligands will be small.

In this way it can be shown that the infinite sum in (6.1) in reality consists only of a few large terms.

Both in a ligand substitution and in a reductive elimination one of the ligands must leave the complex. This can be described only by a stretching motion. The contribution from the B_{1g} -mode was shown above to be unimportant. (The argument that it describes the dissociation of two ligands and therefore can be excluded is not relevant, because we are only discussing the initial stage of the reaction). The only other stretching motion is of E_u -mode, and it will be shown below that this is a possible reaction path. This does not exclude an active participation of the bending motions. They can facilitate the penetration by the incoming ligand of the complex without any initial stretching. A comprehensive discussion (largely based on the criteria by Salem³⁴) shows that all motions except A_{2u} and the two E_u 's are negligible. Here we will only discuss why these three latter motions are expected to be large.

From Fig. 4.1 and 4.2, it can be concluded that possible LUMO:s are $3b_{1g}$ and (especially in PtX_4^{2-}) $2a_{2u}$ and $4e_u$. The HOMO:s are the d-levels ($3a_{1g}$, $2e_g$ and $2b_{2g}$) and ligand $p\sigma$, $p\pi||$ and $p\pi\perp$. Only a few of these fulfil the symmetry requirements imposed by the motions, however. For bondmaking and -breaking those describing σ -bonds are most important. They are lying in the plane and have their maxima along the metal-ligand axis (cf. Appendix 2 Fig. A 2.1 (a)). They are of the symmetry species B_{1g} ($2b_{1g}$ and $3b_{1g}$) and E_u ($2e_u$).

In the following treatment, it will sometimes be necessary to discuss PtX_4^{2-} and PdX_4^{2-} separately, because of the difference in electronic energy levels, cf. Fig. 4.1.

The out-of-plane A_{2u} -motion "selects" the orbital pair $(3a_{1g}, 2a_{2u})$ in PtX_4^{2-} . It is obvious that they will impose a large change in the electron density above and below the plane of the nuclei and therefore are likely to be involved in the promotion of the A_{2u} -motion (in conformity with this the high intensity ($\epsilon = 9 \cdot 10^3 \text{ cm}^{-1} \text{ M}^{-1}$) of the band assigned $2a_{2u} \leftarrow 3a_{1g}$ implies that these orbitals are localized in the same region of space). Because the denominator in (6.1) is larger for these orbitals in PdX_4^{2-} than in PtX_4^{2-} the A_{2u} -motion is simpler to activate in the latter complex. In PdX_4^{2-} the pair $(b_{2u}, 3b_{1g})$ is possible by symmetry and also for energetic reasons. However, the out-of-plane b_{2u} -orbital is not located near to the in-plane $3b_{1g}$ (cf. the discussion in section 4.4) and a large influence on the A_{2u} -motion is unlikely.

For PtX_4^{2-} it is also possible to have the combination $(2e_g, 4e_u)$. It is less efficient than $(3a_{1g}, 2a_{2u})$ for two reasons. Firstly, $2e_g$ is out-of-plane, whereas $4e_u$ is in-plane. Secondly, the term diagram in Fig. 4.4 and the discussion in section 4.2 shows that $E_o(A_{1g}) - E_k(A_{2u}, 3a_{1g}, 2a_{2u})$ is lower than $E_o(A_{1g}) - E_k(A_{2u}, (2e_g)^3 4e_u)$ by approximately $1.2 \text{ } \mu\text{m}^{-1}$.

The bending and stretching motions of E_u -symmetry in PdX_4^{2-} are connected with the orbitals $(3e_u, 3b_{1g})$ and $(2e_u, 3b_{1g})$. Schematically, the former pair will promote only the bending mode and the latter the stretching one, but in reality no such sharp distinction is possible. We can conclude that if an energetic impact is made on $2e_u$ and/or $3e_u$, then both motions will be activated.

That the stretching motion and the connected pair $(2e_u, 3b_{1g})$ will make a large contribution to the reaction path is obvious (cf. ref. 6, p. 267f). As already shown in the discussion about intensities in section 4.4, both $2e_u$ and $3b_{1g}$ are located between the moving nuclei. $2e_u$ describes σ -bonding and $3b_{1g}$ σ -antibonding.

Concerning PtX_4^{2-} , the energetically most favourable orbitals should be $(2e_g, 2a_{2u})$. Other possibilities, though probably less favourable, are $(1e_g, 2a_{2u})$, $(2b_{2g}, 4e_u)$ and $(3a_{1g}, 4e_u)$.

However, neither of these combinations are very useful. It seems plausible that the empty $4e_u$ -orbitals are of mainly metal-p-character and the lower ones $(2b_{2g}, 3a_{1g})$ are mainly of metal-d-type. Thus, by the same argument as for the B_{1g} -motion, their interaction with the E_u -bending motion must be slight. Especially, $3a_{1g}$ and $4e_u$ are mainly out-of-plane and in-plane, respectively, which makes this combination less useful.

Concerning the pairs $(1e_g, 2a_{2u})$ and $(2e_g, 2a_{2u})$, their transition densities correspond to a change of the electron density over and below the plane. Even if this will influence the in-plane E_u -stretching, it will probably not be so effective as $(2e_u, 3b_{1g})$. It should be remarked, however, that the energy difference, (in PtCl_4^{2-}) of the denominator of expression (6.1) is at least $6.4 \mu\text{m}^{-1}$ (cf. section 4.2) for the pair $(2e_u, 3b_{1g})$ but only $4.3 \mu\text{m}^{-1}$ for $(2e_g, 2a_{2u})$. Thus, the latter may contribute to the sum in (6.1) as much as $(2e_u, 3b_{1g})$.

The selected E_u -stretching motion consists of two components (cf. Fig. 6.1). When one of these is activated, the complex will change its symmetry (cf. ref. 6, p. 268) from D_{4h} to $C_{2v}(C_2^-)$ (i.e. the C_2 -axis of C_{2v} is identical with one of the in-plane C_2^- axes of D_{4h}). The doubly degenerate $E_u(D_{4h})$ -motion is then split into two different symmetry species. One of these, $B_1(C_{2v})$, describes the antisymmetric stretch vibrations of the cis-ligands. The other, $A_1(C_{2v})$ (the totally symmetric one) describes the inward motion of the trans-ligand and the outward motion of the leaving ligand according to Fig. 6.2.

As a consequence of the symmetry splitting of the E_u -

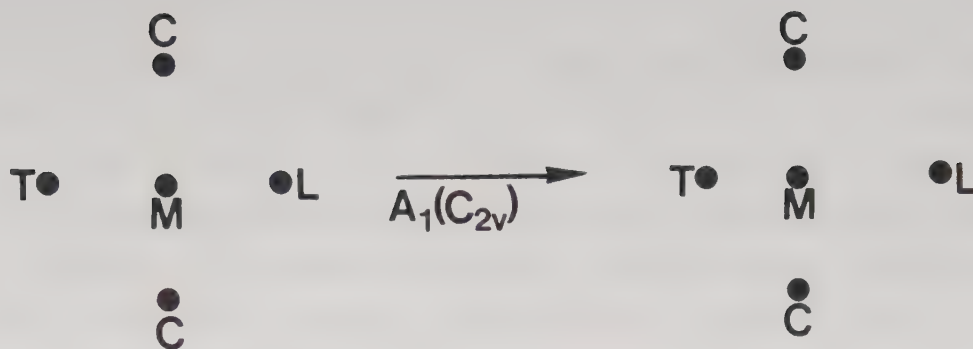


Fig. 6.2 Symmetry changes due to the x-component of the E_u -motion. C denotes cis, L the leaving and T the ligand trans to L. M is either Pd or Pt.

species, transition densities of the same species are also split into A_1 and B_1 .

This splitting is also obtained (without any motion) if the two ligands T and L are unequal (say $T = I^-$ and $L = H_2O$). In this case the orbitals with the doubly degenerate symmetry species E_u and E_g in D_{4h} -complexes (i.e. $L = T$) are split in the following way

$$E_u(D_{4h}) = A_1(C_{2v}) + B_1(C_{2v})$$

$$E_g(D_{4h}) = A_2(C_{2v}) + B_2(C_{2v})$$

cf. Appendix 2 Fig. A 2.1. This means that the σ -bonding $2e_u$ -orbitals are split into an a_1 -component describing the σ -bonds along the T - M - L-axis and a b_1 -component along the C - M - C-axis. A similar situation occurs for $3e_u$. The out-of-plane π -bonding and -antibonding $1e_g$ - and $2e_g$ -orbitals are split into a_2 -components along the C - M - C-axis and b_2 -components along the T - M - L-axis. (Of course, no such splitting occurs for the orbitals with non-degenerate symmetry species (D_{4h}). Thus, the $2b_{1g}$ -orbital (cf. Appendix 2) describes σ -bonding between the central metal atom and all the four ligands irrespective of whether T and L are

equal or not). That some orbitals describe bonds mainly between trans ligands is essential for an understanding of the so-called trans-effect. This will be discussed in section 6.4.

It should be remarked that the E_u -motion implies that a dissociative mechanism is symmetry allowed. Whether it occurs or not depends on energetic factors. Pearson (ref. 6, p. 268) has shown that this sort of mechanism is unlikely because of loss of ligand field stabilization energy (the $2b_{1g}(d_{xy})$ -orbital is raised in energy). Another reason is the increase in energy of the $p\sigma$ -orbital of the leaving ligand. This can be estimated from Fig. 4.1. In $PdCl_4^{2-}$, the $2e_u(p\sigma)$ -orbital is stabilized with approximately $0.8 \mu m^{-1}$ vs. the non-bonding b_{2u} -orbital (and twice as large as compared to the in-plane non-bonding a_{2g} -orbital). A spontaneous dissociation is thus not likely.

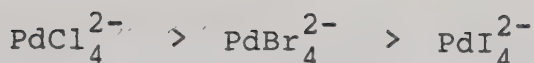
6.3. General predictions about reactivity

For the selected initial reaction path of E_u -stretch-species the state wave-functions involved are of A_{1g} - and $E_u((2e_u)^3 3b_{1g})$ -symmetry species, respectively. As emphasized earlier (section 4.2) the spectral assignments indicate that the energy difference $E_k(E_u((2e_u)^3 3b_{1g})) - E_o(A_{1g})$ probably is about $2 \mu m^{-1}$ larger for $PtCl_4^{2-}$ than for $PdCl_4^{2-}$. In agreement with this (cf. expression (6.1)), the reactivity of the former complex is much less than that of the latter, the ratio being approximately $1:10^5$ (cf. ref. 4 (c) Table VII). (In principle, trends in $\Delta G^\ddagger$ -values should be compared rather than rate constants).

The well-known trend in reactivity



also conforms with this theory: The energy difference between $^1A_{1g}$ and $^1E((2e_u)^3 3b_{1g})$ is



(it is 4.50, 4.06 and 3.75 μm^{-1} respectively, cf. Fig. 4.4). The numerator of (6.1) $\langle \psi_0(^1A_{1g}) | \partial U / \partial Q | \psi_k(^1E_u) \rangle$ will change only slightly between the complexes. This can be inferred from the small changes in molar absorptivities for $3b_{1g} \leftarrow 2e_u$ (cf. Appendix 1, Table A 1) and the expected correlation between the intensity of a dipole-allowed spectroscopic transition and a motion where $\partial U / \partial Q$ is of the same symmetry species as the relevant dipole component (cf. Larsson ref. 35, p. 38). As in the spectra, triplet states (formally $\langle \psi_0(^1A_{1g}) | \partial U / \partial Q | \psi_k(^3E_u) \rangle$), will contribute strongly in PdI_4^{2-} , but not in PdCl_4^{2-} . Thus, the energy decrease according to (6.1) will be larger for PdI_4^{2-} than for PdCl_4^{2-} , which means that PdI_4^{2-} should be expected to react faster than PdCl_4^{2-} .

It should be remarked that it is not possible to discuss any reactivity trends among the mixed aqua-halide complexes, because it has not been possible to observe the transition equivalent to $^1E_u \leftarrow ^1A_{1g} (3b_{1g} \leftarrow 2e_u)$ in their spectra. The transition energies increase above 5 μm^{-1} (below 200 nm) already for $\text{PdCl}_3(\text{H}_2\text{O})$, cf. IV Fig. 5. This implies that the reactivity of such complexes should decrease, but the effect of the ionic charge of the complex and the distorted electron density (if L and T in Fig. 6.2 are unequal) render predictions difficult.

The difference in ionic charge between AuCl_4^- and PdCl_4^{2-} also makes a comparison of the reactivities of these two complexes difficult. However, the bands corresponding to the transition $^1E_u \leftarrow ^1A_{1g} (3b_{1g} \leftarrow 2e_u)$ lie close to each other for PdCl_4^{2-} (4.50 μm^{-1} ; cf. IV Table II) and AuCl_4^- (4.39 μm^{-1} ; cf. Elding and Gröning ref. 25, Table 7), whereas the corresponding band for PtCl_4^{2-} probably has an energy of at least 6.4 μm^{-1} (cf. section 4.2). We can then conclude that the reactivity order should be



Even if no direct comparison is possible it is obvious that the values given by Elding^{4(a,b)} for platinum(II)- and palladium(II) mixed aqua-halide complexes and for platinum(II) and gold(III) mixed chloro-bromo-complexes²⁵ are in qualitative agreement with this conclusion.

6.4. Transition densities and the trans-effect

The transition densities with an E_u symmetry species correspond to a number of orbital pairs. The most essential of these are probably $(2e_u, 3b_{1g})$, $(1e_g, 2a_{2u})$ and $(2e_g, 2a_{2u})$. As shown in section 6.2 the transition density of E_u symmetry species can be divided into its $C_{2v}(C_2')$ -components A_1 and B_1 . The former describes changes in the electron density along with or parallel to the T - M - L-axis (the initial reaction path) in Fig. 6.2 and the latter one the density along the C - M - C-axis. Schematically it is thus possible to discuss changes in the bonds along these two axes as if they were independent of each other. It is not possible, however, to make a further division into independent changes in the T - M and M - L bonds, respectively; instead all changes are extended over all these three atoms. Qualitatively it is thus possible to understand that the electronic structure of T may affect the rate of replacement of L by another ligand i.e. the trans-effect. From the symmetry properties of the molecular orbitals involved it can be concluded that the effect can be subdivided into three cases.

The first one, due to the pair $(2e_u, 3b_{1g})$, describes changes coinciding with the T - M - L-axis i.e. changes in the σ -bonds between these atoms. The second one, given by the pairs $(1e_g, 2a_{2u})$, $(2e_g, 2a_{2u})$ describes changes parallel to the T - M - L-axis above and below the plane i.e. changes in the out-of-plane π -bonds. The third one, is a similar effect in the in-plane π -bonds given for instance by the pair $(3e_u, 3b_{1g})$. There is thus a natural division of the effect into a σ - and a π -trans-effect, respectively.

The equality between ($2e_u$, $3b_{1g}$) with the usual description of the σ -trans-effect is not obvious. The reason is that the upper empty molecular orbital used in the conventional description of the σ -effect^{33,36} is composed of metal p-orbitals. According to Langford and Gray³³ these are the only metal orbitals involved in σ -bonding which have simultaneously trans-directional properties. Now, this is not quite true. The metal $d_{x^2-y^2}$ -orbital is also involved in σ -bonding ($2b_{1g}$, cf. Appendix 2) and it has the advantage of being the most easily accessible empty orbital (i.e. $3b_{1g}$) of correct symmetry. The lowest energy empty molecular orbital with σ -antibonding properties described by the metal p-orbitals is $4e_u$. The relative energies (in PtX_4^{2-} -complexes) of the empty levels $3b_{1g}$, $2a_{2u}$ and $4e_u$ can be estimated from Fig. 4.4 (b) by the terms ${}^1A_{2g}(3b_{1g} \ 2b_{2g})$, ${}^1B_{1u}(2a_{2u} \ 2b_{2g})$ and (the hypothetical) ${}^1E_u(4e_u \ 2b_{2g})$. Their energies are (in $PtBr_4^{2-}$, where they all occur simultaneously) 2.42, 3.03 and $4.63 \ \mu m^{-1}$, respectively, cf. ref. 20 Table X. Thus, the $4e_u$ -level lies approximately $2 \ \mu m^{-1}$ above $3b_{1g}$ and is accordingly less important. It is appropriate here to remark that the presence of the $4e_u$ -orbital means that the number of transition densities with symmetry species E_u which can influence the reaction may be large. Since the energy difference between $4e_u$ and the filled orbitals is larger than that between $2a_{2u}$ and the filled orbitals, all transition densities where $4e_u$ is invoked can be neglected in a descriptive treatment like the present one. In a computational treatment all transition densities of correct symmetry species (E_u) must of course be invoked.

It could be argued that the participation of the $3b_{1g} (d_{x^2-y^2})$ -orbital in the electronic process should make cis ligands almost as labile as trans ligands (cf. ref. 37, p. 139). This is not so, however, because one effect of the splitting of orbitals of E_u -symmetry species will be to maintain a non-influenced σ -bonding orbital of $B_1(C_{2v})$ symmetry species for the cis ligands. These will not depart appreciably from their ground-state positions along the C - M - C-axis.

The energy difference between $2e_u$ and $3b_{1g}$ is lower in PdX_4^{2-} than in PtX_4^{2-} . Accordingly, the σ -trans-effect gives a larger contribution to the total trans-effect in the former complex. Even though the trans-effect is a property of the complex and not of a single ligand it seems plausible to conclude that the decrease in energy difference between $2e_u$ and $3b_{1g}$ in the series



corresponds to a trend in the σ -trans-effect according to



It is easily shown that the out-of-plane π -trans-effect given by the pair $(2e_g, 2a_{2u})$ is identical with the π -trans-effect originally suggested by Chatt and coworkers.³² According to their proposal, the effect is due to the presence of high-lying filled metal atom orbitals (d_{xz} i.e. $2e_g$, cf. ref. 32, p. 4459f) and low-lying empty ligand orbitals with a symmetry involving change of sign when reflected in the plane. In the present case it corresponds to ligand p_z -orbitals of A_{2u} symmetry species. It is generally agreed that the contribution from the halide ligand p_z to the $2a_{2u}$ molecular orbital is unimportant. Accordingly, the contribution to the π -trans-effect from the pair $(2e_g, 2a_{2u})$ is unimportant as far as halide ligands are concerned. The pair $(1e_g, 2a_{2u})$ might of course make a contribution which will increase in the series



According to the assignments, the $2a_{2u}$ -level lies nearer to the d-levels in platinum(II) than in palladium(II) complexes. This means that the (out-of-plane) π -trans-effect will be more important for the former complexes, cf. also Chatt et.al. ref. 32, p. 4460. This has the interesting implication that ligands expected to give a strong π -trans-

effect (but a small σ -trans-effect) in platinum(II) complexes, may show a low trans-effect in palladium(II) complexes. An example of such a ligand might be ethylene.

The in-plane π -trans-effect is given by the pair ($3e_u$, $3b_{1g}$). In platinum(II)-complexes it is also possible that the $4e_u$ -orbital takes part. It is reasonable to believe that the effect might be important in palladium complexes because the energy difference between $3e_u$ and $3b_{1g}$ is smaller for these complexes than for those of platinum(II).

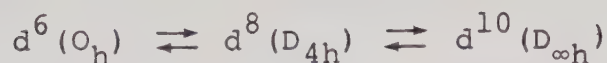
It should be emphasized that both for platinum(II) and palladium(II) complexes the σ - and π -trans-effects can be introduced from the theory solely via the E_u -stretching motion; no other motions will make this possible.

Obviously, the σ -trans-effect is more fundamental than the π -trans-effect, because it promotes bond-breaking between the central metal atom and the leaving ligand. During the inward motion of the trans-ligand T, the $3b_{1g}$ ($d_{x^2-y^2}$)-orbital has to accept electrons. It can be occupied by at most two electrons. This extreme case corresponds to reduction of the central metal atom (filled d-shell). It is hardly possible that one single halide T-ligand can supply both electrons, so another electron donor must also be present. The leaving ligand L dissociates and is not replaced. Thus, reductive elimination discussed in the following section, can be regarded as a limiting case of the proposed σ -trans-effect ($2e_u$, $3b_{1g}$). Therefore, it will also be possible to describe the reductive elimination reaction by the E_u -stretching motion and the transition density given by the pair ($2e_u$, $3b_{1g}$).

6.5. Redox processes

Schematically, reductive elimination and oxidative addition are described by a change of the number of d-electrons around the central metal atom, and by a change of coordina-

tion number. The reactions and the symmetries of the complexes involved can be written as

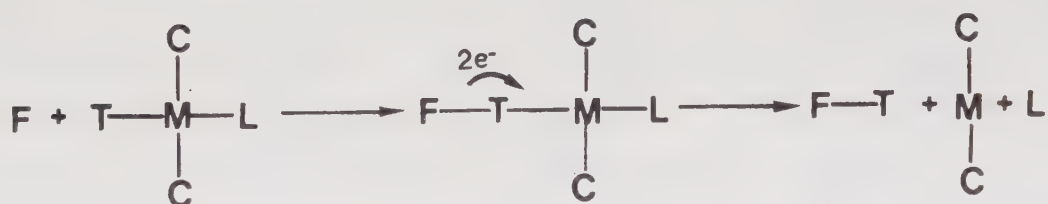


and exemplified by the couples platinum(IV) - platinum(II) and gold(III) - gold(I), respectively.

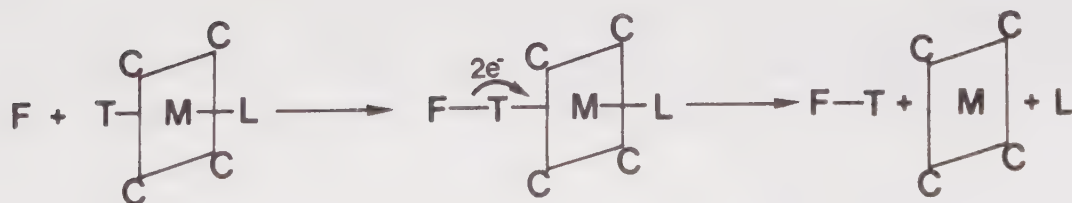
The intimate mechanism for reductive elimination suggested by a number of authors for square-planar gold(III)^{38,39} and octahedral platinum(IV)^{2,40} complexes is closely connected with the σ -trans-effect ($2e_u$, $3b_{1g}$ in $d^8(D_{4h})$). The mechanism describes the reduction by two consecutive steps. Initially, there is an attack by a free halide of sufficient reductive power on one of the halide ligands of the complex followed by the electron transfer. This is accompanied by bond-breaking so that both the halogen molecule formed and the trans-ligand dissociate. The lowest empty d-orbital on the metal atom (LUMO) which can accept two electrons is $3b_{1g}(d_{x^2-y^2})$ in square-planar gold(III) and the empty orbitals of E_g symmetry species (i.e. d_{z^2} and $d_{x^2-y^2}$) in octahedral platinum(IV). The HOMO is, as shown at the end of section 6.4, the ligand $p\sigma$ of E_u symmetry species in gold(III) and T_{1u} species in platinum(IV), respectively. Thus, the transition density in platinum(IV) is of $T_{1u}(O_h)$ -symmetry species ($= E_u(D_{4h}) + A_{2u}(D_{4h})$). Therefore, in the reverse process, i.e. oxidation of platinum(II) (d^8 , D_{4h}) to platinum(IV) (d^6 , O_h), the transition density is either of the E_u - or A_{2u} -symmetry species. The former corresponds to an attack by a halogen molecule on one of the halide ligands of the complex. This cannot result in oxidation (but possibly reduction, cf. III and the hypothetical reduction by diiodochloride plus chloride). The only possibility is thus the A_{2u} transition density. This means that the halogen molecule attacks along the z-axis i.e. above the plane, so that the metal atom and the two atoms of the halogen molecule lie on a straight line, which is perpendicular to the plane of the complex. For the complex

the HOMO is $3a_{1g}$ (d_{z^2}) and LUMO is $2a_{2u}$ and for the halogen molecule the HOMO is the σ_g -orbital of highest energy and LUMO is σ_u . The most important orbitals are obviously the electron-donating $3a_{1g}$ and the electron-accepting σ_u .

As far as reduction is concerned, it is always possible to find a filled orbital with correct symmetry on a free halide ion which can interact with a $p\sigma$ -orbital on the halide ligand of the complex. The free ligand (abbreviated F) will approach the complex along the T - M - L-axis in Fig. 6.2. This is the most favourable path for the incoming ligand to promote electron transfer to the $3b_{1g}$ (D_{4h}) or e_g (O_h) orbital. The activated complex (or short-lived intermediate formed) will have the geometric configuration according to Fig. 6.3:



(a)



(b)

Fig. 6.3 Possible mechanism for the reduction of a square-planar (D_{4h}) complex (a) and an octahedral (O_h) complex (b), respectively, by a free halide ligand F. The other ligands are denoted according to Fig. 6.2. See also ref. 2.

If the F-ligand is a good electron donor and T a good bridging ligand the electron transfer will be facilitated. The latter explains why reduction of AuBr_4^- by I^- is faster than that of AuCl_4^- . This can also be seen in another way: the orbitals $2e_u$ and $3b_{1g}$ differ less in AuBr_4^- than in AuCl_4^- . According to ref. 25 Table 7 the difference for corresponding states, is $3.92 \mu\text{m}^{-1}$ for the former and $4.39 \mu\text{m}^{-1}$ for the latter complex.

From symmetry considerations Pearson⁶ has proposed an alternative mechanism for square-planar redox reactions. In the specific case discussed here it assumes that AuCl_3I^- is formed in an initial substitution process and the reaction proceeds via an E_u -bending motion so that the halogen molecule (ICl) is formed from I and Cl cis to each other.

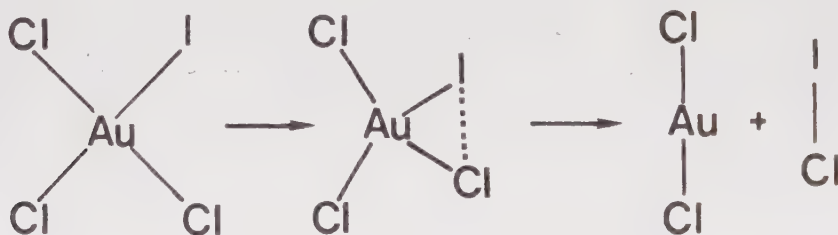


Fig. 6.4 Reduction of gold(III) in an intramolecular reaction.

Contrary to the mechanism in Fig. 6.3 (a) this involves a rather extensive rearrangement of the ligands.

Pearson (ref. 6, p. 287, Fig. 10) showed that the reverse process is prohibited by a rather high energy barrier, because one filled d-orbital has its lobe in the I-Cl-bond and therefore will be raised in energy. If this argument is applied to the reduction in Fig. 6.4 it means that the E_u -bending must be strongly activated; it is hardly possible for the ground-state AuCl_3I^- to react. There

are no such problems connected with the alternative mechanism proposed in Fig. 6.3.

It is appropriate to remark here that the suggested intramolecular mechanism where the trans-ligands T and L in Fig. 6.2 are converted to the halogen molecule (cf. for instance Ford-Smith et.al.⁴¹) is not symmetry allowed (cf. Pearson ref. 6, p. 286).

The application of the theory for PtX_4^{2-} is straightforward. As shown earlier, the transition density must be of A_{2u} symmetry species which corresponds to the HOMO $3a_{1g}(d_z^2)$ and LUMO $2a_{2u}$ of the complex. Another possibility is to choose the σ_u -orbital of the halogen molecule as the LUMO. This has no consequences for the mechanism or for the predictions about rate differences between PtX_4^{2-} and PdX_4^{2-} . According to the assignments, the $2a_{2u}$ -level lies considerably nearer to $3a_{1g}$ in PtX_4^{2-} than in PdX_4^{2-} . As discussed in section 4.3 the d-levels are more extended in space for platinum(II) complexes than for those of palladium(II). It does not matter which of these arguments we use since according to both the oxidation of platinum(II) should be faster than that of palladium(II). The rates for oxidation of PtCl_4^{2-} and PdCl_4^{2-} by Cl_2 are in agreement with this conclusion. A comparison between the observed rate constants at equal ligand concentrations indicates that PdCl_4^{2-} is oxidized about 2000 times slower, cf. ref. 31 for PtCl_4^{2-} and ref. 27 for PdCl_4^{2-} .

A similar comparison between the rate of reduction of AuX_4^- and PdX_4^{2-} is not possible. Reduction of the latter is thermodynamically unfavourable and no values seem to have been reported.

6.6. The incoming ligand

The E_u -stretching motion describes only the path of the leaving ligand but says nothing about the path of approach

of the incoming one. It is, however, possible to show how the incoming ligand must interact with the complex in order to activate the E_u -motion. It could be argued that the theory presupposes a small interaction only and therefore cannot describe in detail the intimate mechanism. This conclusion is not necessarily true. For instance the reductive elimination is adequately described by the theory, though the process involves both a large change of electron density and the complete removal both of the halogen molecule formed and of the ligand trans to it.

It will be shown below that the symmetry approach cannot give an unambiguous mechanism, because the dissociation of the leaving ligand as given by the E_u -motion can be combined with the motion of the incoming ligand in more than one way. Clearly, the derived π - and σ -trans-effects mean that the conventionally adopted mechanism^{32,33} is in conformity with the symmetry discussion here. These effects show how the E_u -motion can be activated.

For the platinum(II) complexes the E_u -motion is promoted by an oblique approach so that the $2e_g$ (or rather one of its components, say d_{xz}) is influenced, i.e. the transition density given by the pair ($2e_g$, $2a_{2u}$) is operative. It means that this mechanism is based upon the presence of the π -trans-effect. If there are ligands involved without any π -trans-effect, but with a strong σ -trans-effect (say hydride) then the E_u -motion must be activated via the $2e_u$ -orbital - i.e. the transition density given by the pair ($2e_u$, $3b_{1g}$) is operative. The same is true for the palladium(II) and gold(III) complexes considered here, because the $2a_{2u}$ -orbital is less accessible. The problem is that any influence from an attacking ligand on the $2e_u$ -orbital is sterically hindered by the leaving ligand. This can be circumvented in at least three ways. For instance Basolo et.al.⁴² showed that the so called electrostatic polarization theory could give a satisfactory explanation for the platinum(II)-complexes. At least for the palladium(II)

and gold(III) complexes the presence of the E_u -bending motion is probably important (cf. page 32). The incoming ligand might attack nearly in the plane rather than perpendicular to it. Finally, another alternative, which might be possible at least in principle, is similar to the reductive elimination process, cf. Fig. 6.3 (with F = incoming ligand). If the $3b_{1g}(d_{x^2-y^2})$ orbital contains less than two electrons when the interaction is at its maximum, dissociation of L would be possible, without reduction occurring. Instead, another ligand will replace L, and F dissociate. This is analogous to the so-called halide-assisted substitution suggested by Gustafson for platinum(IV) complexes (ref. 2 p. 20 and Fig. 1 c path k_8 k_3 k_5).

However, there is experimental evidence that this latter mechanism can hardly describe ligand substitution processes in square-planar complexes. In a study of the gold(III) halide-thiocyanato-system by Elding, Gröning and Gröning³⁹ they found that both substitution of a halide by thiocyanate and reduction by the latter was possible. The substitution process was faster than the reduction. Moreover, they could convincingly show that the reductive elimination process was not intramolecular (cf. Fig. 6.4), but was better described as an intermolecular process according to Fig. 6.3(a).

It is hardly possible that both reactions could occur according to nearly the same mechanism, in this case the intermolecular one (cf. Fig. 6.3(a)). It seems more likely that two different mechanisms are operating. Obviously this makes an intermolecular substitution process for these square-planar complexes less probable.

There is, however, the alternative that F in Fig. 6.3(a) is a solvent molecule (cf. Fig. 6.5). This is probably a common situation, because of the large excess of solvent compared to all other species. If the E_u -motion is not merely an excited vibration, but the initial stage of a reaction there must also be an

incoming ligand present in a correct position. Obviously the experimental rate constant will be proportional to the product of concentrations of the incoming ligand and the solvent. The latter varies only slightly even with a large change (say from 0 to 1 M) in the former. Therefore, the rate depends only linearly on the concentration of the incoming ligand.

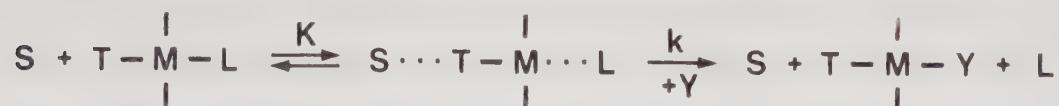


Fig. 6.5 Possible mechanism for a square-planar substitution reaction. S is a solvent molecule. The other ligands are denoted according to Fig. 6.2.

$$\text{RATE} = k_{\text{sol}} \left[\begin{array}{c} | \\ T-M-L \\ | \end{array} \right] [Y] \text{ with}$$

$$k_{\text{sol}} = kK[S]$$

Such a process means that the incoming ligand does not react with a complex in its ground-state configuration, but with a complex which has already achieved an amount of activation energy. The mechanism thus assumes a more specific participation of the solvent in the ligand substitution process than is usually assumed.

7. SUMMARY

1. The kinetic and spectral properties of platinum(II), palladium(II) and gold(III) chloro, bromo and iodo complexes have been interpreted in terms of the symmetry and the relative energies of a few active orbitals. The same energy level diagram (cf. Appendix 2, Fig. A 2.2) is assumed to be valid for all the complexes as far as the order of increasing energy of the molecular orbitals is concerned.

2. The observed differences, in both absorption spectra and rates for ligand substitution and redox reactions, between AuX_4^- and PdX_4^{2-} on one hand and PtX_4^{2-} on the other ($X = Cl, Br$ and I) can be explained if it is assumed that the relative energies of the filled and empty molecular orbitals are different between the two groups. This difference is also consistent with the theory (the relative importance of the relativistic as compared to the electrostatic effects).

3. The interpretation shows that a trans-effect is to be expected for square-planar ligand substitution reactions. It can be naturally divided into a σ - and a π -effect. The former is closely connected with one of the possible mechanisms for reductive elimination reactions of these complexes.

4. From the symmetry properties of a few active orbitals it has been possible to show in which ways the square-planar complexes may be influenced by other species in order to promote a reaction. This suggests a few possible mechanisms for reductive elimination and ligand substitution processes, respectively.

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APPENDIX 1.

The absorption maxima and molar absorptivities for the high-intensity bands of PdX_4^{2-} and PtX_4^{2-} , $\text{X} = \text{Cl}, \text{Br}$ and I are given in Table A 1 below. Corresponding term diagrams are displayed in Fig. 4.3 (a) and (b), respectively.

The spectra of PtBr_4^{2-} , PdI_4^{2-} and PtI_4^{2-} have been analyzed using a least-squares program assuming symmetrical Gaussian band shapes. The spectra of PtCl_4^{2-} , PdCl_4^{2-} and PdBr_4^{2-} have been recalculated using the same program. There are only minor differences as compared to the values given in IV, Tables III, IV and V.

The values for PtBr_4^{2-} are based on the spectrum published by Elding and Gröning,²⁰ and their assignment is retained. For PdI_4^{2-} the spectrum published in II, Fig. 1 is used.

Concerning PtI_4^{2-} , the spectrum was obtained by dissolving about 100 mg of K_2PtCl_4 (Johnson and Matthey) in 1 dm³ of 0.10 M NaI (Merck Suprapur) and 0.90 M NaClO_4 (Baker's p.a. recrystallized once). A stable spectrum is obtained within two hours. If the solution is kept in the dark and under nitrogen its spectrum does not change within one month. An increase of the iodide concentration to 1 M gives only a slight change in the spectrum, whereas the change is large if the iodide concentration is lowered (below say 0.010 M). A possible explanation is that $\text{Pt}_2\text{I}_6^{2-}(\text{aq})$ is formed under the latter circumstances. It should be remarked that the spectrum obtained, when K_2PtCl_6 is dissolved in 0.10 M NaI, is completely different.

The bands at $3.75 \mu\text{m}^{-1}$ in PdI_4^{2-} , $3.78 \mu\text{m}^{-1}$ in PtI_4^{2-} and $4.63 \mu\text{m}^{-1}$ in PtBr_4^{2-} are seen only as shoulders on the strong absorption bands from $\text{I}^-(\text{aq})$ and $\text{Br}^-(\text{aq})$, respectively. The quoted values are therefore not very exact.

None of the iodo complexes display any d-d-bands. These are probably hidden under the charge transfer bands.

Table A 1. Wavenumbers, $\lambda^{-1}/\mu\text{m}^{-1}$, and Molar Absorptivities, $\epsilon/\text{cm}^{-1} \text{ M}^{-1}$, for PdX_4^{2-} (aq) and PtX_4^{2-} (aq),
X = Cl, Br and I.

PdCl_4^{2-}	PdBr_4^{2-}	PdI_4^{2-}	Assignment	Excited state
4.50 (29000)	4.06 (26000)	3.75 (22000)	$3b_{1g} \leftarrow 2e_u$	1E_u
-	3.73 (4800)	3.19 (15800)	"	3E_u
3.58 (10300)	3.04 (10300)	2.47 (10000)	$3b_{1g} \leftarrow 3e_u, b_{2u}$	$^1E_u, ^1A_{2u}$
-	2.74 (3500)	2.03 (4100)	"	3E_u
2.9 (200)	2.35 (660)	1.79 (1400)	$3b_{1g} \leftarrow a_{2g}$	$^1B_{2g}$
-	-	1.54 (320)	"	$^3B_{2g}$
PtCl_4^{2-}	PtBr_4^{2-}	PtI_4^{2-}	Assignment	Excited state
-	4.63 (7300)	3.78 (12500)	See page 22	
4.65 (9050)	3.73 (8000)	3.02 (7500)	$2a_{2u} \leftarrow 3a_{1g}$	$^1A_{2u}$
4.34 (7200)	3.41 (2400)	2.59 (4700)	$2a_{2u} \leftarrow 2e_g$	1E_u
3.79 (400)	3.18 (1000)	2.32 (1400)	$2a_{2u} \leftarrow 2b_{2g}$	$^1B_{1u}$

APPENDIX 2.

Symmetry properties of the molecular orbitals.

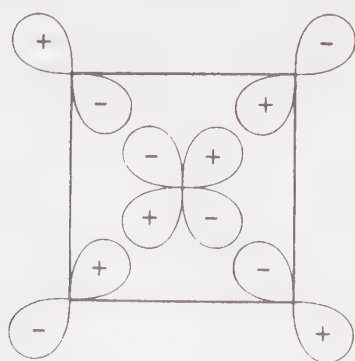
The molecular orbitals are approximated by the usual method of linear combinations of atomic orbitals (LCAO). The directional (symmetry) properties of the latter are shown in Fig. A 2.1 (a), (b) and (c) below. Ligand orbitals (only the p-type are shown) have been adapted to the D_{4h} symmetry. The notations $p\sigma$, $p\pi||$ and $p\pi\perp$ have the following meanings:

$p\sigma$: Ligand p-orbitals lying in the plane and directed towards the central metal atom. They describe σ -bonds. Fig.A2.1 (a).

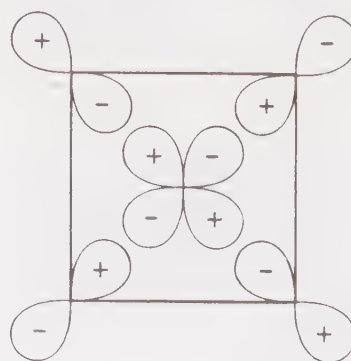
$p\pi||$: Ligand p-orbitals lying in the plane and directed perpendicular to the ligand-metal atom axis. They describe in-plane π -bonds. Fig.A2.1 (b).

$p\pi\perp$: Ligand p-orbitals directed perpendicular to the plane (and hence to the ligand-metal axis). They describe out-of-plane π -bonds. Fig.A2.1 (c).

To most of the symmetry adapted ligand orbitals, but not all, there are metal atom orbitals of the same symmetry. They combine to form a bonding and an antibonding orbital. One example will be treated: take the ligand p-orbitals of symmetry species B_{1g} . They can only combine with a metal orbital having the same symmetry properties, in this case $d_{x^2-y^2}$ cf. Fig. A 2.1 (a). The result is two new orbitals (called $2b_{1g}$ and $3b_{1g}$) according to the following figure:

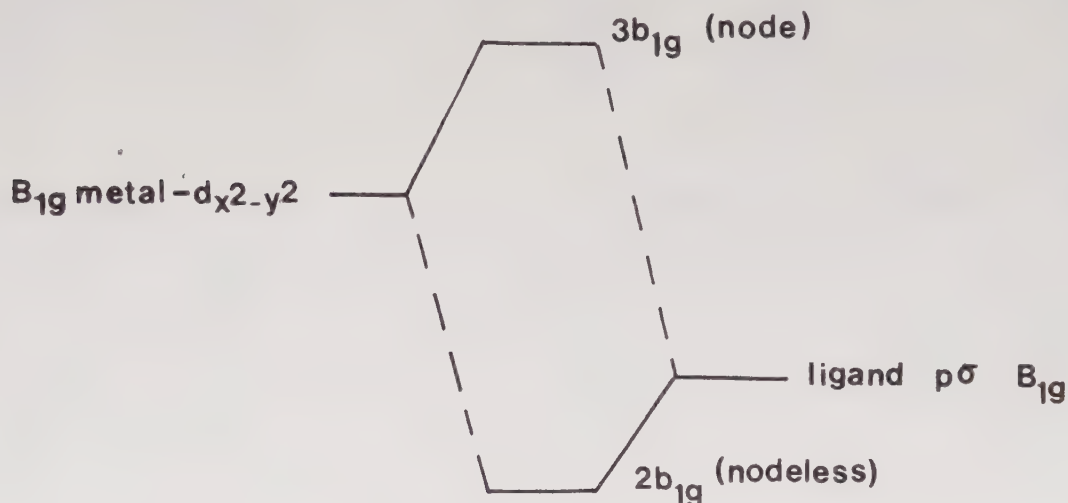


σ -bonding
combination
 $2b_{1g}$



σ -antibonding
combination
 $3b_{1g}$

The $2b_{1g}$ -orbital describes a high electron density on the four metal-halide bonds (there are no intervening nodes) or, in other words, it is the σ -bonding combination. Conversely the $3b_{1g}$ -orbital has one intervening node on each metal-ligand bond, it corresponds to σ -antibonding. The bonding (nodeless) combination has a low energy, whereas the anti-bonding has a high one. The result is as follows:



The molecular orbitals $2b_{1g}$ and $3b_{1g}$ are approximated by the sum

$$2b_{1g} = C_{21} (\text{ligand } p\sigma) + C_{22} d_{x^2-y^2}$$

$$3b_{1g} = C_{31} (\text{ligand } p\sigma) + C_{32} d_{x^2-y^2}$$

where $|C_{21}| > |C_{22}|$ and $|C_{31}| < |C_{32}|$ (cf. ref. 14, Table 1).

The principles of combinations and designations of orbitals are the basis for the energy level diagram in Fig. 4.2.

The numbers preceding b_{1g} (i.e. 2 and 3) establish the energy ordering, i.e. the lower the number the lower the energy (the combination designed $1b_{1g}$ consists of ligand s-orbitals).

In all cases except for the doubly degenerate symmetry species (i.e. E_u and E_g) the symmetry adaption is unambiguous. However, for the two E_u possibilities (i.e. $p\sigma$ (E_u) and $p\pi$ (E_u)) it is always possible to choose one set of $p\sigma$ - and another of $p\pi$ -orbitals, simply because no symmetry

operations can transform any ligand $p\sigma$ -orbital to a ligand $p\pi$ -orbital.

The orbitals most fundamental for both the spectroscopic and mechanistic discussion are:

$2e_u$	i.e.	ligand $p\sigma$
$3e_u$	"	" $p\pi$
$3b_{1g}$	"	metal $d_{x^2-y^2}$
$2e_g$	"	" d_{xz}, d_{yz}
$2a_{2u}$		metal and ligand p_z .

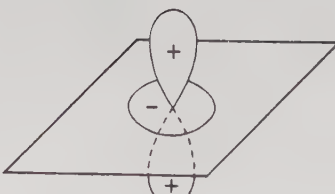
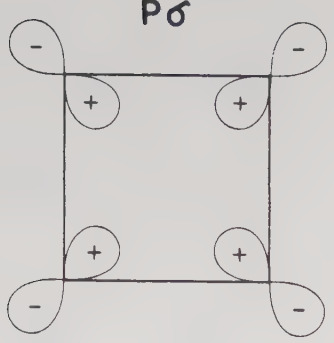
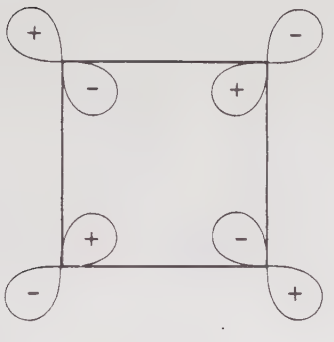
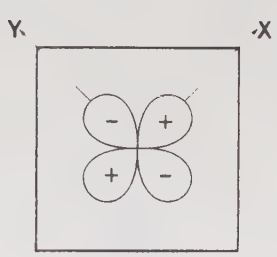
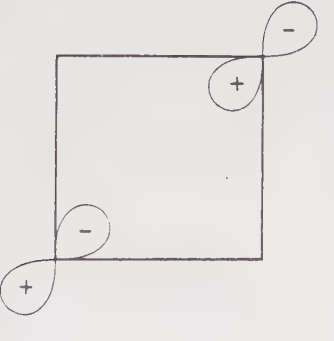
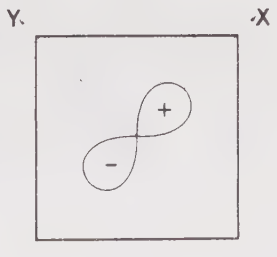
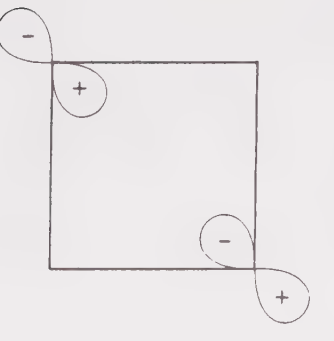
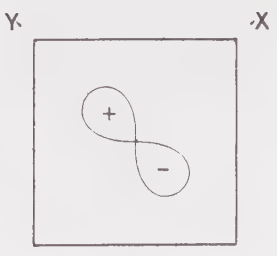
Ligand orbitals (symmetry adapted)	Metal orbital	Symmetry species
$P\sigma$		D_{4h} $C_{2v}(C_2')$
	d_{z^2}	A_{1g} A_1
		B_{1g} A_1
		A_1
		E_u
		B_1

Fig. A 2.1(a) Symmetry properties of the σ -orbitals.

Ligand orbitals (symmetry adapted)	Metal orbital	Symmetry species	
$P\pi$		D_{4h}	$C_{2v}(C_2)$
	None	A_{2g}	B_1
		B_{2g}	B_1
		E_u	B_1
			A_1

Fig. A 2.1(b) Symmetry properties of the in-plane π -orbitals.

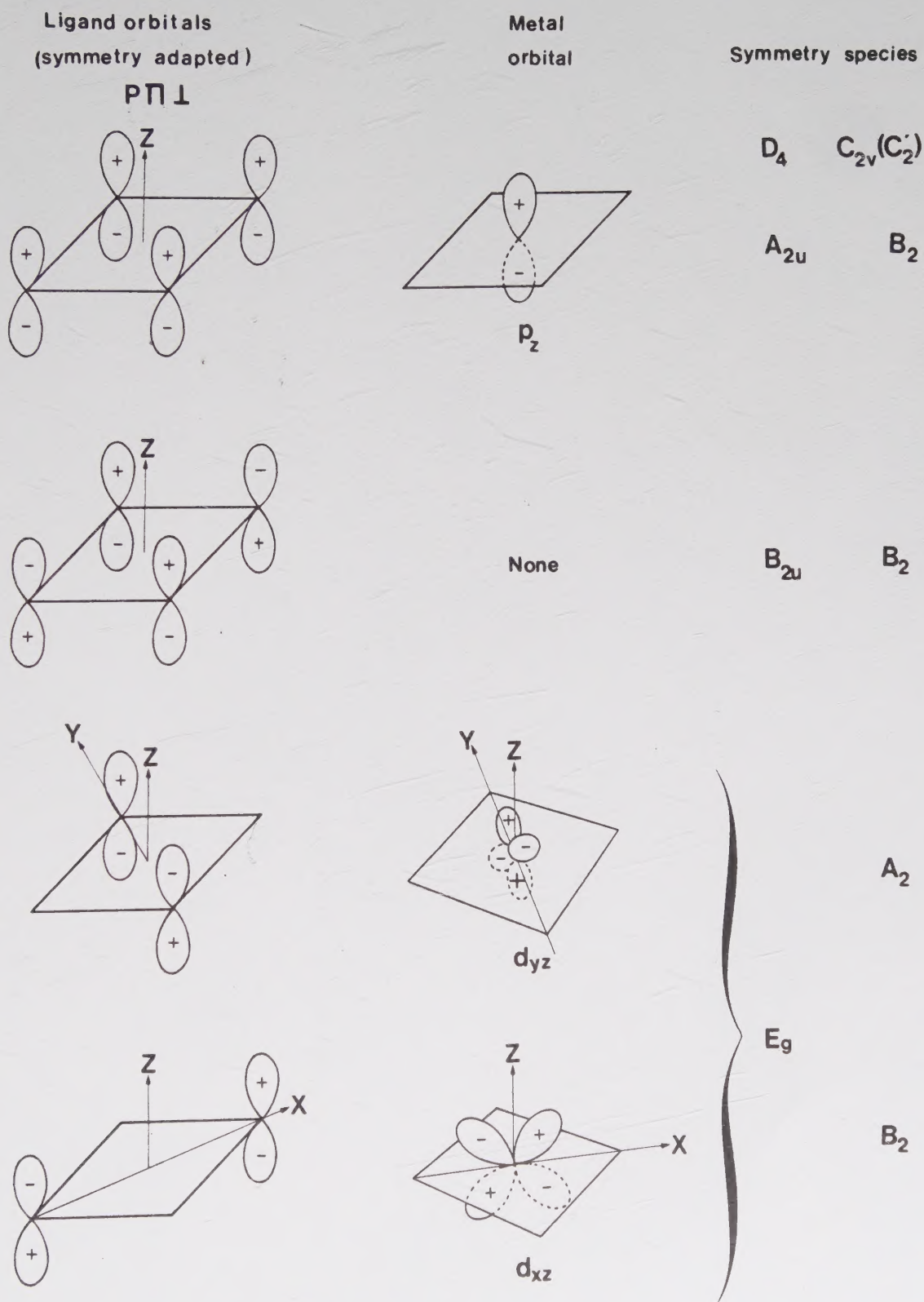


Fig. A 2.1(c) Symmetry properties of the out-of-plane π -orbitals.

